

Anomalous Power Laws of Spectral Diffusion in Quantum Dots: A Connection to Luminescence Intermittency

Taras Plakhotnik,^{*} Mark J. Fernée, Brad Littleton,[†] and Halina Rubinsztein-Dunlop

School of Mathematics and Physics, The University of Queensland, St Lucia, 4072 QLD, Australia
Centre for Quantum Computer Technology, The University of Queensland, St Lucia, 4072 QLD, Australia

Christian Potzner and Paul Mulvaney

School of Chemistry and Bio21 Institute, The University of Melbourne,
Parkville, 3010 VIC, Australia

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We show that the wandering of transition frequencies in colloidal quantum dots does not follow the statistics expected for ordinary diffusive processes. The trajectory of this anomalous spectral diffusion is characterized by a \sqrt{t} dependence of the squared deviation. The behavior is reproduced when the electronic states of quantum dots are assumed to interact with environments such as, for example, an ensemble of two-level systems, where the correlation times are distributed according to a power law similar to the one generally attributed to the dot's luminescence intermittency.

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Semiconductor quantum dots (QDs) are often called “artificial atoms” because of their atomlike wave functions and characteristic discrete energy levels [1]. However, the physics of QDs are much more diverse than the physics of real atoms. In particular, QDs display the phenomena of spectral diffusion and photoluminescence (PL) intermittency [1] or blinking. PL intermittency is observed in the time dependence of the PL intensity. The intermittency manifests itself as unpredictable interruptions of the bright periods in the PL. Although similar effects can be observed in atoms when they enter into metastable states [2], the statistics of “on” and “off” periods in the case of QDs are profoundly different from those of real atoms. The probability of observing an off or on period is proportional to its duration raised to a power between -1.2 and -2 (see reviews [3–6]). Such a power law, called the -1.5 law, covers a huge time scale from tens of nanoseconds to tens of seconds [7] and is quite unusual. In contrast, the statistics of on and off periods in atomic luminescence intermittency are well described by an exponential distribution which is characterized by a lifetime [2]. A theoretical explanation of power-law statistics is a difficult task. Historically, photoionization of QDs was the first mechanism evoked to explain blinking [1]. The on-off statistics were directly related to relaxation and/or random diffusion of the charge carrier. More recently [8–10], it has been suggested that trapped holes or electrons may quench the QD PL. The PL yield, and hence the PL intensity, will then depend on changes in the trapping probability (related to dynamics of the surface atoms).

Spectral diffusion (SD) is another phenomenon common to QDs [11] and other quantum systems, such as single molecules [12], observed as temporal fluctuations of the

wavelengths of their optical transitions. A Stark shift of the transition wavelength caused by applied electrical fields has been measured in QDs, and, consequently, SD has been attributed to chaotic electrical charge displacement in their surroundings [13,14]. It has been found that SD depends on the intensity and the wavelength of the laser radiation used for photoexcitation of QDs; therefore, a model was proposed where the energy difference between the absorbed and reemitted photons is transferred initially to crystal phonons, which then displace the atom or charge distribution on the surface of the QD [15]. At cryogenic temperatures, we have recently shown that such charge hopping occurs with very low probability in some QDs and that individual events can be distinguished in data measured with 1 s time resolution [16].

There are quite appealing similarities in the theoretical descriptions of blinking and SD. For example, both depend on microscopic displacements of atoms or electrons in QDs. But unlike the case of blinking, the QD stays on all the time and therefore the dynamics can be accessed via the statistics of the SD more directly than via the statistics of on and off periods, which indicate only the end points of one type of dynamics. A first experimental observation connecting blinking and SD was made by Neuhauser and coauthors [17], who reported correlations between luminescence intermittency and SD. Recent papers [18,19] that question whether Auger recombination is responsible for quenching luminescence during off states refer to spectral-diffusion-controlled blinking, as has been suggested in a number of theoretical models [8,9,20–22]. Notably, following Ref. [15] there has been little experimental work on the statistics of SD in QDs. In all reports (see also [23,24]), SD did not show any dramatic abnormalities and was quite ordinary.

Empedocles and Bawendi [15] measured the average full width at half maximum (FWHM) of the QD emission lines at temperatures between 10 and 40 K as a function of the integration time. These early experiments were done on CdSe dots overcoated with a nominal 0.7-nm layer of ZnS. The experiments were analyzed by Frantsuzov and Marcus [9] and very satisfactorily explained within the framework of classical one-dimensional random walk with a parabolic bias, which causes the linewidth to exponentially approach a maximum value on time scales of the order of 100 s. At short times, the variance of the transition frequency is proportional to t , the integration time as expected for conventional diffusion. It is then curious that the complex environment needed to explain the power-law blinking dynamics is not somehow manifest in the statistics of SD. Given that many blinking models involve SD, it is clear that such models would benefit from any new insight into the dynamics of SD.

We have experimentally investigated SD in three types of highly luminescent QDs comprising CdSe cores overcoated with different monocrystalline shell structures using advanced epitaxial growth methods. Two types of dots, Invitrogen ITK605 and ITK655 with core radii of 2.5 and 4.0 nm, respectively, are CdZnS-shell commercially available dots studied by several groups [16,19,25–28]. The third type of QD, here labeled CdSe608, was synthesized according to single ion layering techniques [29] using a 3.27-nm core and a shell comprising a single monolayer of CdS and four monolayers of ZnS [30]. The experimental apparatus is described elsewhere [16], and here we list only its most essential characteristics. The spectral resolution of the spectrometer was 80 μeV (5 times better than in Ref. [15]), the base temperature in the cryostat was about 3 K, and the power density of the laser light was in the range of 28–65 W cm^{-2} , well below the saturation intensity of QDs and close to the lowest values used in earlier research on SD and blinking [15]. The SD has been measured on time scales between 1 and 3000 s. This time scale is more than 10 times wider than the ones used earlier [15]. Thus, the experimental settings (in part) and the QDs (in particular) were significantly different from those in Ref. [15]. The investigated dots exhibited very few off events. On average, just one off event was detected per 200 s but the particular dots employed in this study did not blink during the whole measurement until a single terminating off event occurred, from which they did not recover. SD was measured on isolated QDs by collecting a few thousand successive spectra $I_k(\omega)$, $k = 1, \dots, N$, each typically averaged for 1 s.

We have then added a number of consecutive spectra to obtain a series of $N - p + 1$ spectra $\bar{I}_n^{(p)}(\omega) \equiv \sum_{k=n}^{n+p-1} I_k(\omega)$ integrated over p seconds. There is a correlation between $\bar{I}_n^{(p)}(\omega)$ and $\bar{I}_m^{(p)}(\omega)$ if $|n - m| \leq p$, but this approach generates up to $N + 1 - p$ time-dependent spectra similar to those used in Ref. [15]. Although such spectra sometimes exhibited quite irregular shapes, they were

fitted with a Gaussian $\bar{I} \propto \exp[-(\omega - \omega_0)^2/\sigma^2]$ and characterized by a linewidth defined as the FWHM of the fitted Gaussian. We have also directly calculated standard deviations for the spectral line shapes $\bar{I}_n^{(p)}(\omega)$. The result of this analysis is presented in Fig. 1, where the histograms of FWHM_n , $n = 1, \dots, N + 1 - p$, for a number of p values and the corresponding mean values $\langle \text{FWHM} \rangle$ for these histograms are plotted. Although the observed power law with an offset (see Fig. 1 and its caption) is remarkably different from $\langle \text{FWHM} \rangle \propto [1 - \exp(-t/\tau)]^{1/2}$ reported in the literature [9] and is of interest, the power exponent is sensitive to the evaluation procedure and the spectral range used (a 2-meV range centered at the peak intensity was used to determine the linewidth in Fig. 1). Note that if the lines are Lorentzian, then the standard deviation diverges with increasing spectral range. On the contrary, the average transition frequency ω_n calculated as weighted average $\omega_n = \int I_n(\omega)\omega d\omega$ was a robust measure independent of the spectral range. Therefore the SD was characterized by the averaged time-dependent squared frequency displacement defined as

$$D^2 \equiv (N - p)^{-1} \sum_{n=1}^{N-p} (\omega_{n+p} - \omega_n)^2, \quad (1)$$

where the time is represented by p . We assume $\omega(t)$ to be a stationary stochastic function. If $\langle \omega(t)^2 \rangle$ is not diverging, then the expectation value $\langle D^2 \rangle = 2\langle \omega(t)^2 \rangle - 2\langle \omega(t + \tau)\omega(t) \rangle$. Thus $\langle D^2 \rangle$ is related to the autocorrelation function. If the correlations $\langle (\omega_{n+1} - \omega_n)(\omega_{m+1} - \omega_m) \rangle = 0$ for $m \neq n$, then $\langle D^2 \rangle = p\langle (\omega_2 - \omega_1)^2 \rangle$ and the expectation value of D^2 would increase linearly with time. However, the experimental data shown in Fig. 2 on

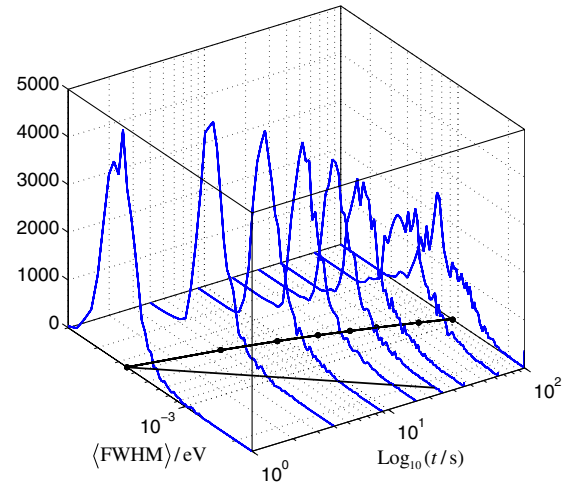


FIG. 1 (color online). Time evolution of the distribution of the FWHM values calculated for a set of moving-average spectra obtained for a single QD. The dots on the “horizontal” plane represent the mean values for the corresponding histograms. The solid line going through the dots is the curve $\langle \text{FWHM} \rangle = [0.30 + 0.15(t/s)^{0.31}]$ meV. A line $\langle \text{FWHM} \rangle \propto (t/s)^{0.5}$ is shown for comparison.

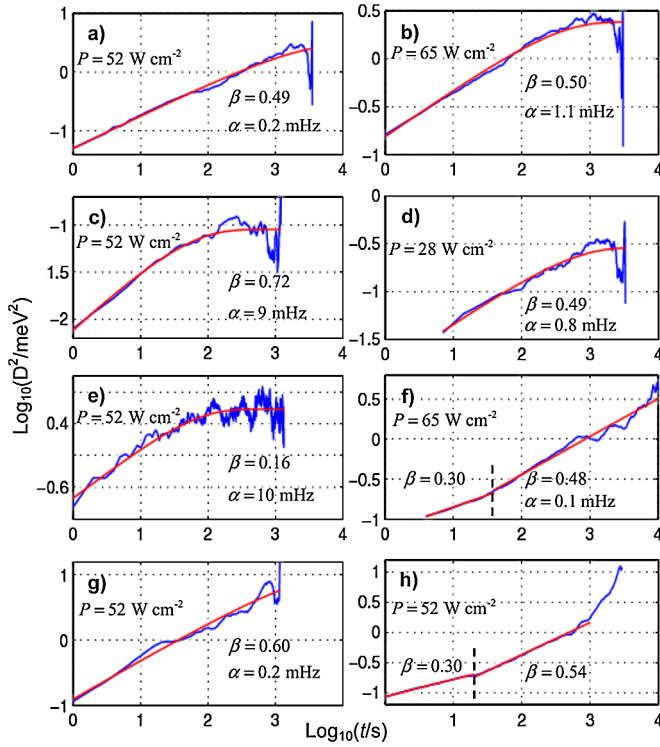


FIG. 2 (color online). Examples of “sublinear” spectral diffusion observed experimentally are shown together with superimposed theoretical curves fitted by using a least-squares criterion. The corresponding theoretical parameters and the excitation intensities are displayed in the panels. A dominant feature of $\beta \approx 0.5$ is associated with a $-3/2$ power law in Eq. (4). The parameter α indicates the rate at the lower cutoff in the distribution function. The upper cutoff should be at least several hertz to be consistent with experimental data at short times. (a), (c), (e), (g), and (h) show results for 4-nm ITK655 dots, (b) and (d) display diffusion of 2.5-nm ITK605 dots, and (f) represents data for a CdSe608 single dot. The QD shown in (g) is embedded in a poly(methyl methacrylate) film. In (f) and (h), the vertical dashed lines separate the regions with apparently different values of β .

a log-log plot demonstrate that D^2 is proportional to $t^{1/2}$ over time scales exceeding 3 decades in some cases.

An exponential decay is typical for $\langle \omega(t + \tau)\omega(t) \rangle$. An example is a model where a QD interacts with a two-level system (TLS). Models based on TLS environments explain phenomena in various fields of physics including SD of spin resonances and luminescence spectra in amorphous solids [31,32] while interacting TLSs were recently introduced to explain blinking [8]. The TLS relaxation rate from its upper state is k_d , and its excitation rate from the lower state is k_u . The change in the QD transition frequency caused by a change in the TLS state is Ω and is described as a random-telegraph stationary process for which [33]

$$\langle D^2 \rangle = \frac{2k_u k_d}{(k_u + k_d)^2} \Omega^2 \{1 - \exp[-(k_u + k_d)t]\}. \quad (2)$$

A similar expression (with different physical meanings of the decay constant and the amplitude) holds for diffusion of some other degrees of freedom such as continuous reaction coordinates biased by a harmonic potential [20,21]. To obtain the power law that we find in experiments, one has to assume a large number of uncorrelated contributions to $\langle D^2 \rangle$. These contributions add up and yield

$$\langle D^2 \rangle = \sum_{s=1}^S A_s [1 - \exp(-tk_s)], \quad (3)$$

where the subscript s numbers the degrees of freedom. The summation can be approximated by the integral $\int_0^\infty \bar{A}(k)\rho(k)[1 - \exp(-tk)]dk$, where the subscript s is dropped, $\bar{A}(k)$ is the average of A_s over the coordinates having the same value of k_s , and $\rho(k)$ is the probability density of k . Note that when the distributions of A_s and k_s are uncorrelated, $\bar{A}(k)$ is independent of k . The integral expression relates $\langle D^2 \rangle$ to the Laplace transform of $\bar{A}(k)\rho(k)$. Generally, the Laplace transform can be inverted to find $\bar{A}(k)\rho(k)$ using data for $\langle D^2 \rangle$. Instead, we evaluate $\langle D^2 \rangle$ with a trial function

$$\bar{A}(k)\rho(k) \propto \begin{cases} 0 & \text{if } k < \alpha, \\ \frac{1}{k^{\beta+1}} & \text{if } k \geq \alpha, \end{cases} \quad (4)$$

where cutoff α removes a singularity. Integration by parts assuming $\beta > 0$ results in

$$\langle D^2 \rangle \propto \frac{1}{\beta\alpha^\beta} \left(1 - e^{-\alpha t} + (\alpha t)^\beta \int_{\alpha t}^\infty \frac{e^{-u}}{u^\beta} du \right). \quad (5)$$

For all times such that $\alpha t \ll 1$, Eq. (5) predicts $\langle D^2 \rangle \propto t^\beta$ if $\beta < 1$ but $\langle D^2 \rangle \propto t$ if $\beta > 1$. In the special case of $\beta = 1$, $\langle D^2 \rangle \propto -t \ln(\alpha t)$ and is practically indistinguishable from a linear function for a limited range of time. The experimental results shown in Fig. 2 are consistent with Eq. (5). The fitted values of α and β are indicated in the figure. The characteristic $\beta \approx 0.5$ is quite insensitive to the dot’s size and environment [see Fig. 2(g)]. Such insensitivity is reminiscent of the robustness of the power-law blinking.

We did Monte Carlo simulations of the squared frequency displacement (Fig. 3). Frequency trajectories of different lengths were obtained. In the case of 3×10^3 points (note that the experimental data set was of similar length), the deviations of D^2 from the expectation values given by Eq. (5) were comparable to those observed in the experiment. But these deviations were much smaller than experimental if 3×10^4 points were used in calculations of D^2 . This indicates that the time range where the -1.5 power law holds may actually exceed three decades. In agreement with Ref. [16], the probability that none of the TLSs in the generated ensemble conforms to $k_s < 1$ Hz but jumps within a 1-s time window is about 0.2.

Thus we have shown that our data imply coupling of the electronic states of QDs to many degrees of freedom

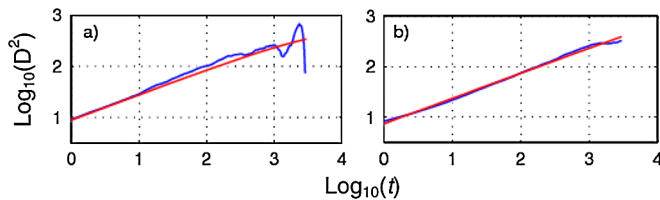


FIG. 3 (color online). Numerical Monte Carlo simulations of the squared frequency displacements. The lengths of the simulated trajectories are 3×10^3 points in (a) and 3×10^4 points in (b). Relaxation rates of 500 TLS are randomly distributed across the range $10^{-5} \leq k_s \leq 10$ so that $\rho(k_s) \propto k_s^{-1.5}$ and $A_s = 2$. The smooth lines are theoretical curves describing the expectation values at $\beta = 0.5$. Large deviations from the expectation values result from the limited length of the data set. These deviations become significantly smaller when the data set is extended to 3×10^4 points.

represented by TLSs or continuous coordinates where the correlation times obey a power-law distribution. This multidimensionality may explain the low blinking rate observed for the reported QDs. For example, some models of blinking [21] invoke an electron-transfer chemical reaction theory [34], which has been recently applied to charge transfer dynamics in QDs [35]. Classically, the transfer occurs when collective nuclear coordinates \mathbf{Q} are near the $(S-1)$ -dimensional intersection $E(\mathbf{Q}) = E'(\mathbf{Q})$ of the two energy surfaces corresponding to the reactant and the product [34]. Within the harmonic approximation, $E(\mathbf{Q}) = \sum_{i=1}^S [k_i^2(Q_i - Q_{i0})^2 + E_{i0}]$ and similarly for $E'(\mathbf{Q})$. If $|Q_{i0} - Q'_{i0}|$ and $E_{i0} - E'_{i0}$ are of the same order for all the coordinates, the potential barrier between the minima of the two surfaces [34] will increase approximately linearly with S , and, consequently, the rate of the electron transfer will decrease significantly. The statistics of blinking may be associated with the statistics of the diffusive return to a subdomain of the S -dimensional space of Q coordinates where the state of the dot becomes unstable. The multidimensionality (as indicated by the SD) is an important factor for such statistics. A robust power law in spectral diffusion processes, experimentally observed on a variety of quantum dots and under various environmental conditions, and the similarities of this power law to the distributions of on and off times in the luminescence intermittency suggest a fundamental connection between these two phenomena. The SD statistics provide complementary information about the physical processes in QDs that cause intermittency. The distribution of the TLS flipping rates should be, for example, factored into the recent theory of blinking [8] where the PL yield depends on changing TLS states. But the statistics that we report here will reshape many models of luminescence intermittency invoking SD.

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*Corresponding author.

taras@physics.uq.edu.au

†Present address: Physics Department, King's College London, WC2R 2LS, United Kingdom.

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