Anomalous transport and memory in quantum dot arrays

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ABSTRACT

We address anomalous transport phenomena in arrays of semiconductor nanocrystals (quantum dots): Transient power–law decay of current as a response to a step in large bias voltage applied across the array, as well as memory effects observed after successive applications of the bias voltage. A novel phenomenological model of transport in such systems is proposed, capable of rationalizing both anomalous transport and memory. The model describes electron transport by a stationary Lévy process of transmission events and therefore requires no time dependence of system properties. The long tail in the waiting time distribution gives rise to a nonstationary response in the presence of a voltage pulse. Noise measurements agree well with the predicted non–Poissonian fluctuations in current. We briefly discuss possible microscopic mechanisms that could cause the anomalous statistics in transmission.

Keywords: Nanocrystal arrays, memory, transient response, anomalous transport, $1/f$ noise, Lévy statistics

1. INTRODUCTION

Semiconductor nanocrystal arrays[1] are important examples of macroscopic systems self–assembled from the nanometer–size building blocks. In such arrays, nearly identical coated semiconductor quantum dots form partially ordered lattices with one or more layers stacked on a substrate (hence the name, quantum dot arrays, or QDAs).

Besides potential applications,[2] dot arrays are compelling since they offer a possibility to control the Hamiltonian by design. This opens new ways to create systems with unconventional transport properties, as well as to study effects of charge ordering and electron–electron interactions.

Despite the progress in synthesis and fabrication of nanocrystal arrays, the nature of electronic transport in them is still unsettled. Proposed theoretical models of transport include mapping of collective dynamics of charges on the dots onto the problem of interface growth,[3] mapping of ordering and correlated hopping of charges on a triangular lattice onto a frustrated antiferromagnetic spin model with long range interactions,[4] as well as a recent generalization[5] of variable range hopping transport in the presense of the Coulomb gap developed earlier for conventional semiconductors.[6]

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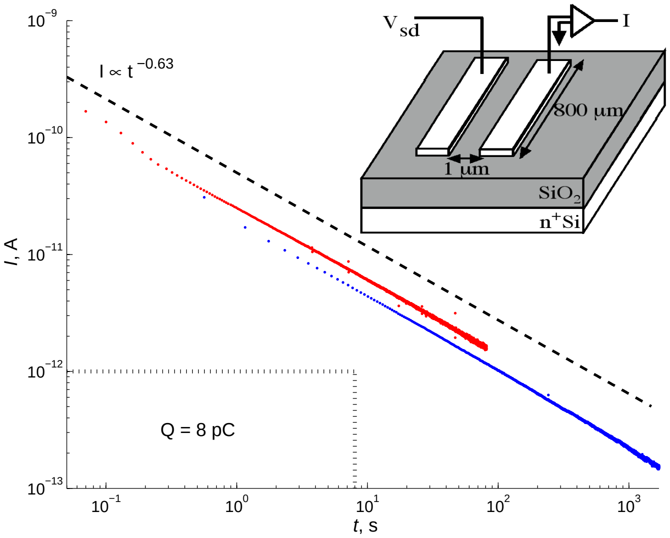

Figure 1. Typical current transient observed in Ref.[7] , with the estimated exponent $\alpha = 0.63$. The lower transient illustrates the memory effect: same exponent α but a lower amplitude I_0. The area in the lower left corner corresponds to the upper bound on the charge capacitively accumulated on the array. *Inset:* experimental setup

2. EARLIER RESULTS IN TRANSPORT IN NANOCRYSTAL ARRAYS

Anomalous transport in QDAs has been extensively studied in Ref.[7] . Below we give a brief summary of the obtained results.

When a negative voltage step is applied to the source at time $t = 0$, with the drain and gate grounded, the following are observed:

(i) A *power law decay* of the current

$$I = I_0\, t^{-\alpha}\ , \quad 0 < \alpha < 1 \tag{1}$$

is always found. The law (1) has been verified to hold for up to five decades in time, from hundreds of milliseconds to tens of hours (Fig. 1).

(ii) This is a true current from source to drain, rather than a displacement current, since the net charge corresponding to (1) diverges with time. Already for observation times $\sim 10^3$ s, the transported charge is orders of magnitude greater than that capacitively accumulated on the array, as shown in Fig. 1.

(iii) The exponent α is *non-universal*. It depends on temperature, dot size, capping layer, bias voltage and gate oxide thickness.

(iv) The system exhibits *memory*: Suppose the bias is off for $t_1 < t < t_2$. The current measured as a function of a *shifted time* $\tilde{t} = t - t_2$ is of the form (1) with an amplitude $\tilde{I_0} < I_0$. This is illustrated in Fig. 1, in which the transient for long times is recorded after that for the shorter time, giving rise to a smaller amplitude. The amplitude $\tilde{I_0}$ is restored, $\tilde{I_0} \to I_0$, by increasing the *off* interval $t_2 - t_1$, by annealing at elevated temperature, or by applying a reverse bias or band gap light between t_1 and t_2.

The response (1) is observed in partially ordered multi–layered arrays of II–VI semiconductor nanocrystals. Each nanocrystal is capped with ∼1 nm coating, so that electrons must tunnel to move between neighboring sites. Although the transient response (1) has been witnessed by a number of groups,[7–11] its origin remains a mystery. It is an important problem, since ohmic conductivity of undoped QDAs is reportedly extremely small.[12] Understanding the nature of the time–dependent response may shed light on the dynamics of carriers in such systems.

It has been suggested earlier that the observed time–dependent current could be a result of time dependence of the state of the system, either because trapping of electrons slows further charge injection from the contact[9] or because of Coulomb glass behavior of the electrons distributed over the nanocrystals.[7] However it might seem quite implausible that system's properties adjust in a coherent fashion over many hours to yield well–reproducible power laws in current over at least five orders of magnitude in time in a broad variety of samples.

The purpose of this work is to suggest an alternative point of view on transport in QDAs, which does not require time–varying system's properties. We propose a model, based on Lévy statistics of waiting times between charge transmission events, in which the system remains *stationary* in a statistical sense, but nonetheless exhibits a transient response. The model is corroborated by the measurements of the spectrum of time–dependent current fluctuations in CdSe QDAs, and a good agreement with the prediction of the model is demonstrated.

In the remainder of this paper we introduce a phenomenological model of transport that agrees with the previous results and yields a certain prediction for the noise spectrum, and then summarize the results of noise measurements and briefly discuss possible microscopic mechanisms that could be consistent with our transport model.

3. MODEL OF TRANSPORT

The key idea of our model is that current (1) can arise in a system described by a *stationary* stochastic process. Taking into account typical sample's aspect ratio $\sim 10^3\,\mu\mathrm{m} : 1\,\mu\mathrm{m}$, we model transport in the dot array by assuming $N \gg 1$ identical independent conducting channels switched in parallel. Each channel is almost always closed, and opens up at random for a short interval τ_0 to conduct a current pulse that corresponds to a unit transmitted charge (as schematically shown in the lower inset of Fig. 2). We further assume that the time intervals between subsequent transmissions are uncorrelated, in which case the channel is completely characterized by the *waiting time distribution* (WTD) $p(\tau)$ of time intervals between successive pulses. The power law decay of the current transient is obtained by postulating that the WTD has a long tail of the Lévy type:

$$p(\tau \gg \tau_0) \simeq \frac{a}{\tau^{1+\mu}} , \quad 0 < \mu < 1 . \tag{2}$$

Note that *all* moments of $p(\tau)$ diverge. The behavior of the WTD at short times, $p(\tau \sim \tau_0)$, is not of interest, since it does not affect the long time dynamics.

The WTD (2) yields the power law decay (1) for the mean value of the current in a single channel with

$$\alpha = 1 - \mu \quad \text{and} \quad I_0 = \frac{\mu \sin \pi\mu}{\pi a} . \tag{3}$$

Qualitatively, the decrease in current with time can be understood as follows. The mean value of the waiting time for the process (2) is *infinite*. Thus if the stochastic process governed by the WTD (2) started infinitely early in the past, the expected value of the current by now would be zero. Turning the bias on at $t = 0$ sets the clock for the process (2). Now, for the measurement interval t, only the waiting times $\tau \leq t$ can occur (as illustrated by the simulation shown in Fig. 2, note the double log scale). Observing the current over a longer time effectively increases the chances for a channel to be closed for a larger time interval, yielding the decay in current, the latter approaching zero at $t \to \infty$. We note that in this transport picture the system's parameters that yield the WTD (2) are *time independent*: The process (2) is *stationary*, i.e. $p(\tau)$ is independent of the measurement time t.

Continuous time random walks characterized by the Lévy WTD arise in various contexts.[13] The main feature of the Lévy statistics is the violation of the central limit theorem. To make contrast with conventional systems, we remind what happens in a Poissonian channel characterized by the finite mean waiting time $\bar{\tau}$. The mean value of the transmitted charge Q grows linearly with time, $\langle Q \rangle = t/\bar{\tau}$, corresponding to a constant current. The variance of the charge is proportional to the mean, $\langle\langle Q^2 \rangle\rangle = \frac{1}{2}\langle Q \rangle$, yielding the decrease of the relative charge fluctuation $\langle\langle Q^2 \rangle\rangle^{1/2} / \langle Q \rangle \propto t^{-1/2}$ in accord with the central limit theorem. Contrarily, in the case of the WTD (2), the mean transmitted charge increases *sublinearly* as $\langle Q \rangle \sim t^{\mu}$, whereas its variance is proportional to the *square* of the mean, $\langle\langle Q^2 \rangle\rangle \propto \langle Q \rangle^2$. Since relative charge fluctuation does not decrease with time, transport in a single channel with the WTD (2) is dominated by large fluctuations (Fig. 2).

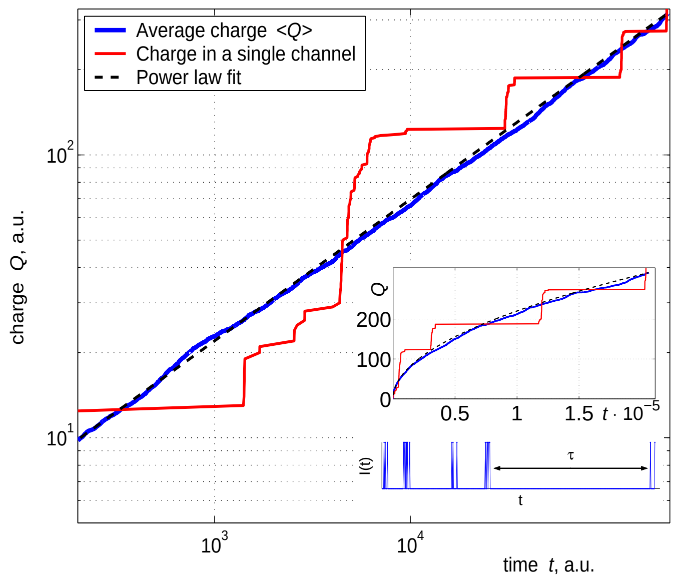

Figure 2. The net transmitted charge $Q(t)$ in a single channel and charge $\langle Q(t)\rangle$ averaged over $N = 100$ channels simulated according to the WTD (2) with $\mu = 0.5$ (plotted in the double log scale). Dashed line is a power law $Q \propto t^{\mu}$. *Inset:* (above) The same plot in the linear scale. The large charge noise in a single channel is due to the lack of self-averaging for a wide WTD. (below) Current in a single channel with a wide distribution of waiting times (schematic). Short current pulses are separated by very long waiting times $\tau \gg \tau_0$.

Although in our model any given channel lacks self–averaging, the charge from $N \gg 1$ independent channels averages to a smooth power law, Fig. 2, with fluctuations reduced by a factor of $N^{-1/2}$. For the typical sample geometry used in our experiments, consisting of *ca.* 50 layers, each layer of $1.6 \cdot 10^5$ dots wide and 200 dots across, one expects large effective N and small current fluctuations, as in Ref.[7] . Furthermore, the average current obtained from the model of independent channels is unchanged even if the channels are not completely identical, corresponding to spatially varying system properties. A simulation shows that the transmitted charge in a system with a flat distribution of the exponent $0.45 < \mu < 0.55$ over a hundred channels yields average charge that is numerically very close to that given in Fig. 2 with $\mu = 0.5$.

4. MEMORY

Memory originates in our transport model in the way that is analogous to aging in the Lévy systems.[14] Because of large typical waiting times $\tau \gg \tau_0$, any given channel is most likely found in a non–conducting state when the voltage is turned off at $t = t_1$. In addition, due to very slow dynamics of channel parameters, the channel state is likely to remain unchanged by the time the voltage is turned back on at $t = t_2 > t_1$. In this case the channel conducts current as if the voltage has not been turned off. However, there is some chance that the channel changes its state (resets) while the voltage is turned off, with a probability $w_{12} \equiv w(t_2 - t_1)$. The function $w(t)$ monotonically grows between $w(\tau_0) = 0$ and $w(\infty) = 1$. The current at $t = t_2$ as a function of a *shifted time* $\tilde{t} = t - t_2$ is a sum over all channels:

$$I(\tilde{t}\,) = (1 - w_{12}) I_0\, (\tilde{t} + t_2)^{-\alpha} + w_{12} I_0\, \tilde{t}^{\,-\alpha}\,. \tag{4}$$

The function $I(\tilde{t}\,)$ has a singular part at $\tilde{t} = 0$ with the amplitude $\tilde{I}_0 = w_{12} I_0$ determined by the reset probability $w_{12} < 1$. For $t_2 \gg \tau_0$, the first (regular) term in Eq. (4) is negligible compared to the second one. The current (4) is dominated by the latter, yielding an apparent suppression of the measured transient amplitude. We have verified that the reset probability $w_{12} = \tilde{I}_0 / I_0$ is indeed a monotonic function of the time with voltage off. For waiting times from 10 s to 10^4 s in between 100 s long transients, we measure $0.65 < w_{12} < 0.85$; $w_{12} \to 1$ when applying a reverse bias, exposing the dots to the band gap light or waiting for longer times.

5. FLUCTUATIONS OF CURRENT

Although the model described above is consistent with previously reported tranport measurements, it needs to be independently justified. We now formulate a prediction of the Lévy process (2) that has to do with the statistics of current *fluctuations*, rather than with current itself. It can be shown that the WTD (2) leads to a non–Poissonian noise

$$\langle\langle I_{-\omega} I_\omega \rangle\rangle \propto \begin{cases} t^{2\mu} \,, & \omega t \ll 1 \;, \\ t^{\mu}\omega^{-\mu} \,, & \omega t \gg 1 \;. \end{cases} \tag{5}$$

Here $I_\omega = \int_0^t dt'\, I(t') e^{i\omega t'}$. The noise (5) is proportional to $\langle I_\omega \rangle^2$ when $\omega \to 0$, and has a characteristic power law spectrum for large frequencies. Note that the Lévy process (2) yields the *same* power laws for the noise (5) at $\omega t \gg 1$ and for the current, $\langle I_\omega \rangle \sim \omega^{-\mu}$, that are not altered after averaging over N channels.

Measurements of noise in nanocrystal arrays have been reported in Ref.[15] . Let us briefly outline the main results of these measurements, with more details found in Ref.[15] .

We have utilized the nanocrystal arrays produced as described in Ref.[7] by self-assembly of nearly identical CdSe nanocrystals, 3 nm in diameter, capped with trioctylphosphine oxide, an organic molecule about 1 nm long. A film of about 200 nm thick of the nanocrystals have been deposited on oxidized, degenerately doped Si wafers with oxide thickness ≈ 200 nm. The experimental setup has been similar to that utilized in Ref.[7] . Gold electrodes, fabricated on the surface before deposition of the QDA, consist of bars 800μm long with separation of 2μm. The sample has been annealed at 300 C in vacuum inside the cryostat prior to the electrical measurements. Annealing reduces the distance between the nanocrystals and enhances electron tunneling.[7]

To measure the noise, we have recorded 200 current transients each $t = 100$ s long. Measurements have been made on a single sample continuously stored in vacuum, inside of a vacuum cryostat in the dark at 77 K. Each current transient is recorded for 100 s with a negative bias of -90 V. These periods of negative bias are separated from each other by a sequence of zero bias for 10 s, reverse pulse of +90 V for 100 s, and zero bias for 10 s, to eliminate the memory effects.[7] We have checked that current fluctuations for a substrate without the QDA are several orders of magnitude smaller than with the QDA.

We have found that the Fourier transform of current, $\langle I_\omega \rangle$, and the noise power spectrum $\langle\langle I_{-\omega} I_\omega \rangle\rangle$, follow the same power law (5) with the exponent $\mu \approx 0.7$ for the particular sample used. Such a behavior has been observed over about two decades in frequencies $f = \omega/2\pi$ available for data recording, from $f \sim 10^{-2}$ Hz to a few Hz.

6. DISCUSSION

Let us now briefly discuss how the Lévy process (2) can arise microscopically. The immeasurably small zero bias conductivity in our QDAs could mean not having enough phonons to relax energy for charge hops. It is then natural to suppose that hops occur only between *aligned* energy levels of the neighboring dots. The WTD (2) with a long tail can be rationalized if the energies of these levels strongly fluctuate in time, with $\mu = \frac{1}{2}$ corresponding to the Gaussian diffusion of energy levels. One can think of at least two reasons for the level fluctuations. First, the energy ~ 0.1 eV due to bias drop dissipated per hop may provide the levels with the necessary energy reservoir. Second, current–induced fluctuations in the electrostatic environment in the absence of screening may result in a random time–dependent chemical potential for each dot.

Continuous time random walks with power law WTDs (2) also arise when the system dynamics is determined by a broad distribution of time scales, e.g. trap escape times in amorphous solids yielding dispersive transport in photoconduction.[16] However, in the case of a constant supply of carriers the current *grows* with time[17] at a constant bias. This is explained by gradually filling in of the traps thus smoothing the potential for the carriers, effectively increasing the sample conductivity with time.

Remarkably, Lévy statistics was recently observed in fluorescence intermittency of *individual* nanocrystals.[18] It is quite possible that further progress in understanding the microscopic mechanism of the anomalous transport can be achieved by establishing a connection between the statistics of fluorescence and of charge transmission in the same sample. This could discriminate between transport due to the nature of the excited state in a single nanocrystal and collective transport phenomena.

7. CONCLUSIONS

To conclude, we presented a novel mechanism for a non–ohmic conductivity in a disordered system. In particular, we showed that a non–stationary current response can arise in a stationary system with the Lévy statistics of waiting times. The model agrees well with the current and noise measurements in arrays of coated semiconducting nanocrystals. Our results suggest that the notion of conductivity in QDAs (used e.g. in[10]) may be ill–defined since the latter implies Poissonian statistics in transmission. We also demonstrated that noise can help to investigate the system even without precise knowledge of its microscopic transport mechanism. The latter is yet to be clarified by further studies.

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