Persistent Coulomb Blockade Across the Metal-Insulator Transition in Nanoparticle Solids

Davis Unruh\textsuperscript{1}, Chase Hansen\textsuperscript{1}, Alberto Camjanyi\textsuperscript{2}, Joel Bobadilla\textsuperscript{2}, Marcelo Rozenberg\textsuperscript{3}, and Gergely T. Zimanyi\textsuperscript{1}

\textsuperscript{1}Physics Department, University of California, Davis CA 95616
\textsuperscript{2}Departamento de Física, FCEyN, Universidad de Buenos Aires and IFIBA, Pabellón I, Ciudad Universitaria, 1428 CABA, Argentina
\textsuperscript{3}Laboratoire de Physique des Solides, CNRS, Université Paris-Sud, 91405, Orsay Cedex, France

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Nanoparticle solar cells have low carrier mobility. Key causes of this low mobility include that (1) the nanoparticle solids are insulators; and (2) the Coulomb blockade. The insulating behavior can be overcome by driving the system across a Metal-Insulator Transition (MIT). However, the evolution of the Coulomb blockade across the MIT has not been analyzed. This paper focuses on the behavior of the Coulomb blockade by analyzing carrier transport in the insulating phase by our Hierarchical Nanoparticle Transport Simulator, and by Dynamical Mean-Field Theory in the metallic phase. Our unexpected result is that the Coulomb blockade persists across the MIT.

Semiconducting nanoparticle (NP) solids have received significant attention recently. The electron wavefunctions are localized on the NPs: a phenomenon called Quantum Confinement. This Quantum Confinement forces the band gap of the electronic states to be inversely proportional to the NP diameter, making the electronic properties of the NPs tunable \cite{1}. This tunability makes NPs attractive for a wide variety of opto-electronic applications \cite{2}, including generation III photovoltaics \cite{3,4}, light-emitting diodes \cite{5}, and field-effect transistors (FETs) \cite{6,7}.

However, the same Quantum Confinement which makes NPs attractive, simultaneously reduces their utility because it also localizes the charges onto the individual NPs, driving the NP solid insulating. This makes charge transport in NP solids inefficient, and hinders the charge extraction from the NP solar cells. These competing effects of Quantum Confinement are sometimes summarized as the Quantum Confinement Dilemma, or QCD.

Charge transport and extraction in NP solids can be improved by driving them from their insulating phase across a Metal-Insulator Transition (MIT) into a conducting, metallic phase. In broad terms, this is a disorder-driven MIT in the sense that the overlap of electron states on neighboring NPs gives rise to a kinetic energy, possibly enhanced by a neck formation, and thus facilitates the inter-NP hopping, while variations in the size, surface and shape of the NPs unavoidably induces disorder. The NP solid can be moved across this disorder-driven MIT by enhancing the kinetic energy at the expense of the disorder, essentially following the scenario of the Anderson localization.

Experimentally, NP solids can be driven across the MIT by various methods, including atomic layer deposition (ALD) \cite{8}, substitutional percolation \cite{9}, chemical doping \cite{10,11}, and photodoping \cite{12}. For example, ALD infilling with metal oxides, such as alumina, can passivate the majority of the trap-like surface states \cite{8}.

Successful ALD infilling experiments fabricated NP solids exhibiting band-like, temperature insensitive, delocalized transport with mobility values exceeding 7 cm\textsuperscript{2}/Vs \cite{8}. Notably, the improved charge transport did not thwart the optical tunability of the NP solids. Based on this and other progress in enhancing transport, a few groups have succeeded in forming NP solar cells with overall power conversion efficiencies approaching 14\% \cite{13,15}, which is quite promising regarding commercial viability.

On the theoretical front, of course there is a vast literature of the MIT in disordered materials and systems \cite{16}. For the particular case of NP solid, Shklovskii et al. developed insightful theories \cite{10}, and our group has published extensive simulations of the MIT, conceptualizing it as a Quantum Percolation Transition \cite{17}.

Another mechanism that tends to suppress transport is the Coulomb repulsion between electrons. This suppression is the most marked at commensurate electron densities, and is referred to as the Coulomb blockade \cite{18,21}. The physics of the Coulomb blockade is well established in the localized insulating phase: close to commensuration, the transition of an electron to most neighboring NPs is blocked by the electrons that already occupy those neighboring NPs. The Coulomb blockade manifests itself in a large reduction of the electron mobility as the electron filling is increased towards a commensurate value, and recovers once the filling passes the commensurate value. Thus, the mobility forms lobes between integer fillings, separated by pronounced minima at those integer fillings. At finite temperatures, the mobility at these minima is reduced but still finite. Transport is a thermally activated process whose gap is controlled by the disorder between integer fillings, whereas at integer fillings the NP charging energy greatly enhances this transport gap \cite{22,23}.

However, to our knowledge, the question has not been studied in depth whether the Coulomb blockade dissolves as the electron wavefunctions delocalize when the NP solid is driven across the disorder-induced MIT, or does...
the Coulomb blockade persist in some form. This question is the central focus of this paper.

In this quest, we developed techniques that are suited to analyze the charge transport on both sides of the MIT, each capable of capturing the Coulomb blockade, should it emerge. On the insulating side, we employed the Hierarchical Nanoparticle Transport Simulator (HiNTS), developed in our group over the years based on a Kinetic Monte Carlo (KMC) framework to model charge transport via single-phonon assisted thermal hopping [17]. On the metallic side, we captured the transport by adapting the Dynamical Mean-Field Theory (DMFT) for multiply-degenerate electron states, following our earlier work [24].

A standard hallmark of the Coulomb blockade suppressing transport is the mobility exhibiting non-monotonic behavior as a function of the electron density, including a series of minima at commensurate, integer electron fillings, and corresponding maxima around half-integer fillings. In our first paper in this field, using an early version of HiNTS, we have already observed the mobility exhibiting a maximum, followed by a dip, as a function of the NP diameter [25]. This result was consistent with the experimental findings of the Law group [26], reporting the emergence of an analogous maximum. Since the volumetric electron densities were kept constant in these simulations, varying the NP diameter was representative of varying the electron filling per NP. However, the origin of this peak remained unexplored, including whether it is caused by a commensuration-related Coulomb blockade that would emerge at integer fillings.

Coulomb Blockade in the Localized Phase In the insulating regime, electron transport is incoherent, characterized by thermally activated hopping in which electrons tunnel from one NP to another. At low temperatures, Efros-Shklovskii [27] or Mott variable range hopping [28] is expected to dominate, while at high (room) temperatures nearest-neighbor hopping is thought to be the primary hopping mechanism [29, 30].

The HiNTS code simulates large samples in a hierarchical manner, thereby overcoming the computational challenges associated with the huge number of degrees of freedom. We implemented this hierarchical approach in the following steps.

(a) We computed the electronic energies of individual PbSe NPs with diameters varying across the 3-8 nm range by using a parameterized band structure model [31].
(b) We then generated a cubic superlattice NP sample by selecting NPs with diameters randomly chosen from a Gaussian distribution of mean $d$ and width $\sigma$, and arranged them in a cubic structure.
(c) We injected electrons into the sample to reach a specified volumetric electron density.
(d) We computed the mobility of an entire sample by a specifically adapted Extended Kinetic Monte Carlo (KMC) algorithm with voltage bias. We applied a sufficiently small voltage bias to ensure the transport remained in the linear regime of the I-V curve. To remove any internal bias resulting from energy disorder, this voltage bias was applied both in the forward and reverse transport directions, and the resulting currents were pairwise averaged.

The emergence of the Coulomb blockade in NP solids can be captured in different manners. Some experimenters explored the behavior of the mobility by systematically increasing the NP diameter [26, 32]. In these cases, as the volumetric electron density was kept constant, the number of electrons per NP increased with increasing diameter. Its noted that changing the diameter also varied other system parameters, convoluting the physics of the Coulomb blockade with other trends.

An alternative experiment would be to vary a gate voltage applied to the NP solid in a FET geometry, isolating the density dependence of the mobility. Such an approach tunes the electron density readily, without impacting the other system parameters.

To make direct contact with the above experimental results, we performed HiNTS simulations of transport across a layered PbSe NP solid, for a sequence of samples where the NP diameter was systematically varied. Fig. 1 shows these results, overlaid against the 2011 experimental results of Kang et al [32], who analyzed PbSe NP solids with an EDT ligand coating. The HiNTS simulation results and the Kang experimental results exhibit a remarkable agreement. Very analogous results were also observed in experiments from the Law group [26].

![FIG. 1: Dependence of conductivity on NP diameter. HiNTS computational results (circles) are compared to experiment results from Kang et al 2011 (squares). The dotted vertical line indicates a filling of 1 e$^-$/NP.](image-url)
Coulomb charging energy of an electron. In our model of PbSe NP solids, the attempt of an electron to hop onto NPs already occupied by another electron is forced to pay an extra Coulomb charging energy when attempting to hop onto NPs that are already occupied by other electrons. This Coulomb blockade emerges because the electrons are repelled by the average on-site charging energy $E_C$ at the commensurate filling of $\frac{e}{NP}=1$ as a function of the energy disorder $D$, normalized by the average on-site charging energy $E_C$. The charging energy is defined as $E_C = \frac{e^2}{2C}$, where $C$ is the effective capacitance. The on-site, or self-capacitive portion of $E_C$ we use is consistent with single NP ab initio calculations and single NP empirical-perturbative hybrid calculations, and the self-capacitive term appearing in experimental reports. Some papers go beyond the on-site term and also include the contribution of the mutual capacitance of nearest neighbor NPs to $E_C$. We caution, however, that for internal consistency, such approaches also need to include the repulsive energy from electrons located on these same nearest neighbor NPs. For the purposes of the present paper, we confine ourselves to on-site Coulomb blockade effects, and will discuss nearest neighbor effects in future work.

In competition with the kinetic increase of the mobility, the electron-electron interactions suppress the transport by the Coulomb blockade in these NP solids as the electron filling approaches commensurate values. This Coulomb blockade emerges because the electrons are forced to pay an extra Coulomb charging energy when attempting to hop onto NPs already occupied by another electron. In our model of PbSe NP solids, the Coulomb charging energy $E_C$ exceeds the thermal energy, $E_C >> kT$. Therefore, the electron hops onto neighboring NPs that are already occupied by other electrons will be blocked as the hops will not have sufficient thermal assistance to overcome the charging energy $E_C$. Approaching half-integer fillings, this blocking will be more and more complete, and thus critically suppresses transport.

Next, we demonstrate the emergence of the Coulomb blockade deconvoluted from kinetic effects and energy variations, both induced by the experimentalist’s choice of varying the NP diameters across a set of samples. In Fig. 2, the diameter of the NPs was kept fixed, and only the electron filling per NP was varied. Keeping the NP diameter fixed removed the exponentially growing background, as well as the variation of the energy levels with the NP diameter. This unmasked that the mobility itself broadly decreases with increasing filling, as the electron transport is more and more hindered by the repulsion of the increasing number of other electrons. As before, this general trend of transport-suppression becomes overwhelming at integer fillings, giving rise to pronounced mobility minima, with accompanying maxima around half-integer fillings. This reconfirms the presence of the Coulomb blockade in this insulating phase of the NP solids.

It is mentioned here that there is ongoing discussion about the magnitude of the “charging energy” of the NP solids. This term is defined differently by different groups. The charging energy is written as $E_C = \frac{e^2}{2C}$, where $C$ is the effective capacitance. The on-site, or self-capacitive portion of $E_C$ we use is consistent with single NP ab initio calculations, single NP empirical-perturbative hybrid calculations, and the self-capacitive term appearing in experimental reports. Some papers go beyond the on-site term and also include the contribution of the mutual capacitance of nearest neighbor NPs to $E_C$. We caution, however, that for internal consistency, such approaches also need to include the repulsive energy from electrons located on these same nearest neighbor NPs. For the purposes of the present paper, we confine ourselves to on-site Coulomb blockade effects, and will discuss nearest neighbor effects in future work.

The simulations in Figs. 1 and 2 reported two scans of the electron filling across commensurate integer values. These scans solidly established the presence of the Coulomb blockade in the insulating phase of NP solids.

In order to study the evolution of the Coulomb blockade as the disorder-driven MIT is approached, we determined the dependence of the mobility at the Coulomb blockade-driven minimum at the commensurate filling of $\frac{e}{NP}=1$ as a function of the energy disorder $D$, normalized by the average on-site charging energy $E_C$. Fig. 3 shows that the Coulomb blockade-driven mobility minimum remains robust over a wide range of disorder values. Central to our thesis, as the disorder decreases towards metallicity, interaction effects become more dominant and the mobility minimum gets deeper as a more perfect Coulomb blockade is achieved. This is a particular case where higher disorder increases mobility, by enabling hopping made otherwise inaccessible by a high charging energy barrier. It is noted that at this commensurate filling, the kinetic coupling energy as defined by $\hbar \Gamma$ (where $\hbar$ is Planck’s constant and $\Gamma$ is the average NP-NP hopping rate) is small compared to both $D$ and $E_C$. The relevant control parameter therefore becomes the ratio of the latter two energy scales, $D$ and $E_C$, as used in Fig. 3.

Crossing the MIT to the metallic phase, HiNTS ceases to be a faithful model of transport, as the electron wave-
functions become extended over an increasing number of NPs, and their phases start to increasingly impact transport. Neither of these factors are captured by HiNTS adequately.

**Coulomb Blockade in the Delocalized Phase:** For the above reasons, we adapt the Dynamical Mean Field Theory (DMFT) to describe transport in the metallic regime. DMFT provides a nonperturbative method to study the interplay between correlation effects and electron banding and has in particular produced insights into the Mott metal-insulator transition.

The NP solid can be thought of as a Hubbard model, whose sites correspond to individual NPs. The electronic states of the sites are chosen to be N-fold degenerate, to capture the degeneracy of the PbSe NPs. While the conduction band states in PbSe NPs have 8-fold degeneracy, for technical reasons we used N=6 in our work. Nevertheless, given the low filling of the bands, n varying only up to n=2, the results are expected to be essentially the same. The NP charging energy \( E_C \) maps onto the Hubbard U interaction term. The ensuing Hamiltonian is then a three orbitals degenerate Hubbard model with intra- and inter-orbital density-density Coulomb interaction U.

Dynamical mean-field theory maps a lattice problem onto a quantum impurity model, a finite-size system coupled to a noninteracting bath of electrons, plus a self-consistency condition. The simulations were performed using the continuous-time quantum Monte Carlo (CTQMC), which samples a diagrammatic expansion of the partition function in powers of the impurity-bath hybridization. In this method the on-site Hamiltonian is solved exactly, and the coupling to the bath is treated by a perturbation expansion.

For the noninteracting electrons we adopt a semicircular density of states of half-bandwidth \( D = 1 \). The Coulomb interaction term is set to \( U/D = 6 \) and the inverse temperature is \( \beta D = 100 \).

Fig. 4 shows the electron mobility of such a degenerate Hubbard model. Three main trends are visible: (1) the mobility broadly decreases with the electron filling \( n \), as the repulsion from the growing density of electrons increases the effective mass of the electrons in a Fermi-liquid sense; and (2) the mobility exhibits maxima around half integer fillings. (3) Most importantly, the mobility exhibits pronounced minima at commensurate integer fillings. This result provides clear evidence that even though in this Delocalized Phase the electron wavefunctions are extended at incommensurate fillings, the Coulomb blockade emerges once again upon approaching integer fillings. This is largely driven by the fact that approaching integer fillings the interactions tend to (re-)localize the generically extended electron wavefunctions, thereby recreating the physics of the mobility-suppressing Coulomb blockade.

Fig. 4 further illustrates this physics via the evolution of the Fermi level \( \mu \) with the electron filling \( n \). The jumps of \( \mu \) at integer electron filling \( n \) indicate the formation of Hubbard gaps and the corresponding localization of the electron wavefunctions.

We note that standard mean field calculations of the N-fold degenerate Hubbard model do not capture the emergence of these mobility minima: only DMFT is powerful enough to do so.

Remarkably, all three features of the mobility, determined by DMFT in the Delocalized Phase, in particular the presence of the Coulomb gap, are closely analogous to...
near half-integer filling levels. 

Signs of NP solar cells and NP optoelectronics should tune the carrier filling well away from commensurate fillings in the Localized Phase on the metallic side of the MIT, thus demonstrating remarkable persistence of the Coulomb blockade across the MIT in NP solids. 

The importance of our central result for optoelectronic and solar applications can be summarized as follows. Two major suppressors of carrier transport in NP solar cells are the NP solid being in its insulating phase, and the Coulomb blockade, driven by strong Coulomb interactions. Transport, and thus charge extraction can be improved by driving the NP solid from its insulating phase through a Metal-Insulator Transition into its metallic phase. 

Improving the carrier transport by driving the NP solid metallic must take, however, into consideration the above-established persistence of the Coulomb blockade. Since the Coulomb blockade is a strong controller of carrier transport even on the metallic side of the MIT, designs of NP solar cells and NP optoelectronics should tune the carrier filling well away from commensurate values via doping or other methods, to preferably remain near half-integer filling levels. 

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Conclusions: The central result of our paper is the remarkable similarity of Fig. 2 and Fig. 4, where Fig. 2 shows the Coulomb blockade-driven minima at commensurate fillings in the Localized Phase on the insulating side of the MIT, while Fig. 4 shows the same Coulomb blockade-driven minima in the Delocalized Phase on the metallic side of the MIT, demonstrating remarkable persistence of the Coulomb blockade across the MIT in NP solids.

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