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A Theoretical Consideration of Disorder in a Finite 1D Metal Cluster Chain in a Nanoporous Solid

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Green's function formalism was developed to study the physical properties of one-dimensional arrangements of ligand stabilized metal clusters intercalated into the channel structure of a nanoporous solid. This approach enables us to formulate the so called partial "solitary'' problem of mesoscopic tunnel junctions similarly to the problem of the behavior of an electron in a one-dimensional tight-binding and in a set of vertically and horizontally random delta-function models. We analytically calculated the potential distribution, taking into account the effects of disorder, which influence the form of the charge soliton. Applied to a channel of a porous solid filled with metal clusters, we discuss that the inter cluster capacitance C as well as the self-capacitance C_0 can fluctuate from site to site, i.e. "vertical'' and "horizontal'' disorder, respectively. It is shown that the knowledge of the potential distribution enables us, in principle to calculate the capacitances and by this the diameter as well as the spacing of the clusters.

Recent advances in chemistry allow the synthesis of well defined nanoscaled objects and of solids with nanoscaled subunits with high reproducibility. To this family of "nanomaterials'' belong on the one hand those objects, the lateral extension of which falls into the size range of a few nanometers. These so called nanoparticles or clusters [1,2] (in the current literature there is no common notification) are much smaller than the characteristic length scales, the de Broglie wavelength, the mean free path and the phase relaxation length expressing itself in the so called size quantization effects or quantum size effects and therefore being described as "quantum dots''. Although these length scales vary widely from one material to another in this size range the dimensionality determines the material properties.

On the other hand also crystalline nanoporous solids have to be included into this classification. The most prominent compounds are zeolites and related structures, which are strongly bounded open framework alumo-silicates, wherein pores or channels of nanometer lateral extension are formed. Those pores are accessible for various guest molecules, making these materials important for many applications, e.g. in catalysis, water treatment and separation processes. Due to their chemical composition these nanoporous solids have wide electronic band gaps, making these materials optically transparent as well as electrical insulators (whereas ionic conductivity is not taken into account) allowing to use these solids as "physically inert'' matrix. Besides this, big efforts are done to synthesize nanoporous semiconductors, as many new physical

properties are expected from this "quantum anti dot" solids, but up to now just a few examples are known [3].

In the case of one-dimensional (1D) structures efforts are done to fill channels with pre-formed, ligand stabilized metal clusters, which consist of defined atom numbers, which form the metal core, and are surrounded by a dielectric ligand shell [4]. In the ideal case an 1D array of identical tunnel junctions inside the host channels result. Here they replace the junctions of conventional single electron tunneling arrays, in which correlated tunneling events may occur, due to the Coulomb blockade effect (see, e.g. [5,6,7,8], and references therein), giving rise to various applications [9,10]. Although these clusters are labeled to be uniform, by nature certain statistical fluctuations in the atom numbers forming the core, have to be taken into account. Effecting a finite size distribution, these deviations will directly influence the self capacitance C_0 of the particles ("vertical" disorder). Furthermore, it will be difficult to realize ideal dense package, i.e. to avoid "horizontal" disorder along the array, which will decrease the junction capacitance C (see Fig. 1).

The aim of this paper is to consider the effect of disorder on the potential distribution in a finite 1D arrangement of ligand stabilized clusters within a uniaxial channel of a porous solid, taking into account a finite size distribution and building defects, like deviations from a perfect linear orientation or void spaces, leading to vertical or horizontal disorder. Both effects have to be taken into account in planing strategies to build SET devices. Due to the similarity to the microscopic solid state problem of local disorder, an exact analytical solution for the potential distribution in terms of Green's function (GF) can be developed [11]. The GF approach enables us to formulate the so called partial "solitary" problem of mesoscopic tunnel junctions similarly to the problem of the behavior of an electron in an 1D tight-binding and in a set of random delta-function models although the real transport of electrons in such arrays is incoherent generally. Applying this to the consideration of a channel in a porous solid filled with metal clusters, the

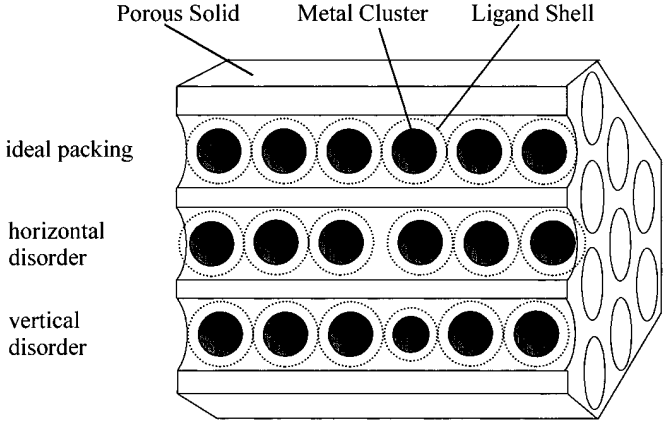

Fig. 1. Schematic drawing of stabilized metal clusters inside the channel structure of a nanoporous solid. Within one chain, the clusters are separated by the thickness of the dielectric ligand shell, whereas the inter particle capacitance C corresponds to the thickness of the ligand shell and the self-capacitance C_0 corresponds to the cluster size. Either C or C_0 can fluctuate from site to site due to horizontal or vertical disorder, respectively

following discussion will be performed with the assumption that (i) either the capacitance C is the same for all junctions whereas the self-capacitance C_0 can fluctuate from site to site due to a finite size distribution, or (ii) C_0 is the same, whereas C can fluctuate from site to site. Further we assume that the metal cluster have a continuous density of states, i.e. we exclude quantum size effects and its influence on the capacitance from our consideration, and host/guest interaction will be neglected. Generally this simplifications and restrictions are not necessary assumptions for the method discussed here, as a general expression allows us to take all these effects into account.

To calculate the potential distribution of the disorder chain of metal clusters we follow closely [11] and will show how the problem of mesoscopic tunnel junctions can be maped to the 1D tight-binding model with a class of periodic Hamiltonians.

In the tridiagonal model for an 1D array of N junctions the only non-zero elements are the diagonal elements $C_{i,i} = C_0$, which are representing the self-capacitance of the islands, and the nearest-neighbor elements $C_{i,i\pm1} = C$, dominated by the tunnel junction capacitance.

The potential $\varphi_i^{(0)}$ can be described by the following set of linear equations, which follow from the charge conservation law

$$-C\varphi_{i-1}^{(0)} + (2C + C_0)\varphi_i^{(0)} - C\varphi_{i+1}^{(0)} = Q_i, \qquad for \quad i = 1, \cdots, N-1. \tag{1}$$

Here we assume that we know the electric charge $Q_i = en_i$ of all electrodes.

The partial "solitary" or single charge soliton solution of Eq. (1), where there is no charge on any of the islands except that a single charge appears on the k-th island, i.e.

$$Q_i = e\delta_{i,k}. \tag{2}$$

can be calculated explicitly. The potential of an arbitrary island i as a function of the distance from the charged k-th island and very far from the edges of the array is given by [12]

$$-\varphi_i^{(0)} = \frac{e}{C_{\text{eff}}}[\Pi(x)]^{|i-k|}, \tag{3}$$

where

$$\Pi(x) \equiv \left(x - \sqrt{x^2 - 1}\right) \tag{4}$$

with $x = 1 + C_0/2C$ and $C_{\text{eff}} = \sqrt{C_0^2 + 4CC_0}$. Note that Eq. (3), which describes the partial "solitary" or single charge soliton solution is correct in the limit

$$-N \ln \Pi(x) \gg 1, \tag{5}$$

i.e. very far from the end of the array.

As for the differential equation for the matrix GF $G(i,k)$ for the periodic tight-binding Hamiltonian operator in the case of an 1D infinite linear chain discretized into a lattice can be written in the form [13]

$$-VG_{i-1}^{(0)} + (2V + \varepsilon_0)G_i^{(0)} - VG_{i+1}^{(0)} - EG_i^{(0)} = \delta_{i,j}. \tag{6}$$

Here we denote the off-diagonal matrix element $\varepsilon_{i,i\pm1}$ of the periodic tight-binding Hamiltonian by V and the diagonal matrix element $\varepsilon_{i,i}$ by $\varepsilon_0 + 2V$. E is the energy and the indices i, k denote points on a discrete lattice.

The GF for this class of periodic potentials can be calculated exactly [13] and we have

$$G^{(0)}(i,k;E) = \frac{1}{\sqrt{(E-\varepsilon_0)^2 - 4V^2}}\Big[y - \sqrt{y^2-1}\Big]^{|i-k|}, \tag{7}$$

where $y = (E-\varepsilon_0)/2V$ and the upper index (0) of GF indicates that the GF is calculated in the case when the system is infinite.

Formally, the corresponding GF $G^{(0)}(i,k;0)$ and therefore the potential $\varphi_i^{(0)}$ of 1D Poisson's equation for the infinite chain of mesoscopic tunnel junctions can be obtained from the Eq. (7) by substituting $E = 0, V = C$ and $\varepsilon_0 = -(C_0 + 2C)$. Then one has (in the following the parameter $E = 0$ will be omitted in the argument of Green's function)

$$G^{(0)}(i,k) = \frac{\varphi_i^{(0)}}{e}, \tag{8}$$

where the $\varphi_i^{(0)}$ is given by (3).

So the calculation of the potential distribution for the realistic geometry of a finite 1D array is reduced to the calculation of the Green's function for the whole system, taking into account all boundary effects (see [14]).

As an example of vertical disorder we calculated the potential distribution for an infinite 1D array which has a segment with N identical self capacitances C_0. After some cumbersome algebra we get an exact expression for the potential distribution $\varphi_i^{(N)}$ ($i = 0$ and $k = N$)

$$-\varphi_0^{(N)} = \frac{e}{C_{\text{eff}}}\left\{\cosh(N\beta) + \left(\frac{\overline{C}}{C_{\text{eff}}}\cosh(\ln \Pi) - \sinh(\ln \Pi)\right)\frac{\sinh(N\beta)}{\sinh(\beta)}\right\}^{-1}, \tag{9}$$

where $\overline{C}$ is the deviation of capacitance from the original value C_0 , i.e. vertical disorder, and

$$\cosh(\beta) = \cosh(\ln \Pi) - \frac{\overline{C}}{C_{\text{eff}}}\sinh(\ln \Pi). \tag{10}$$

We note that the Eq. (10) is the analogous of the electron energy spectrum equation for the 1D Kronig-Penney chain of identical and negative potentials, rewritten for the negative value of energy.

To extend our model to discuss horizontal disorder, where the self capacitance C_0 is kept constant, but the inter cluster capacitance C can fluctuate from cluster to cluster we consider the contact of two semi-infinite arrays. On the left of the contact at $l \le 0$ the capacitance is C_1, and on the right C_2 ($l \ge 0$). Let us suppose that the $\varphi_{li}^{(0)}$ ($l = 1, 2$) (3) for each arrays is known, when the array are infinite. Thus, φ_{1i} the potential distribution in the left-hand half-space is given by

$$\varphi_{1i} = \varphi_{1i}^{(0)}\Big(1 + r_{12}\big[\Pi(x_1)\big]^{-(i+k+|i-k|)}\Big); \qquad i,k \le 0, , \tag{11}$$

where $\Pi(x_1)$ given by Eq. (4) with $x_1 = 1 + C_0/2C_1$. The quantity r_{10} is the reflection amplitude for a soliton passing from the left region into the right region and can be written in the form

$$r_{21} = -r_{12} = \frac{\sqrt{C_0^2 + 4C_1C_0} - \sqrt{C_0^2 + 4C_2C_0}}{\sqrt{C_0^2 + 4C_1C_0} + \sqrt{C_0^2 + 4C_2C_0}}. \tag{12}$$

The first term in the bracket on the right-hand-side of the potential distribution of the semi-infinite array (11) corresponds to direct propagation and the second term to reflection from the boundary. If $r_{12} < 0$ $(C_1 > C_2)$ then there is a decreased probability to return to the initial point, or in other words, such kind of inhomogeneous array can be described as a mirror, where the soliton will interact with his mirror-image soliton (or anti-soliton) and therefore will be attracted [8]. Note that the total amplitude of reflection of a soliton from a finite disordered chain of metal clusters can be calculated in a similar way too. As was shown in [15], this amplitude is directly related to the Landauer resistance, the calculation of which we will publish elsewhere.

The technique of transition from the infinite to the finite case of an array with "vertical disorder" has already been solved in [11] where we illustrated that even in large arrays (80 clusters) the effect of biased electrodes on its edges is still pronounced.

In conclusion, we developed a general expression for the distribution of the potential in a finite 1D array of arbitrary mesoscopic tunnel junctions in terms of Green's function taking into account vertical and horizontal disorder. Applied to the consideration of 1D arrangements of ligand stabilized metal clusters inside the uniaxial channels of a porous solid we are able to discuss the effect of size distribution and packing defects. We proofed the suitability of the method applied to get an access to physical quantities of molecular scaled objects, which are of technical importance, e.g. in the quality control of devices. The results give rise to further extension to find exact expressions of the electrical characteristics, like conductance peak spacing [16] or the Landauer resistance of arbitrary multijunction arrays.

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