Methodology for Simulation of Electronic Transport in Nanocrystal Solids

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Abstract – **We report here a new methodology associating advanced physics of electronic transport in nanocrystal solids and a powerful numerical method: the Accelerated Superbasin Kinetic Monte Carlo. Both allow us to analyze quantitatively conduction in complex disordered nanocrystal structures.**

Keywords -- Hopping transport; electronic transport in disordered materials; silicon nanocrystal solids; accelerated Kinetic Monte Carlo

I. INTRODUCTION

Despite the emergence of nanocrystal solids, especially in optoelectronic applications such as Photovoltaic or LED [1], so far very few attempts have been made to estimate theoretically the carrier mobility in such systems. This paper presents a methodology to simulate hopping transport in 3D nanocrystal solids, including a suitable physical models and a powerful accelerated Kinetic Monte Carlo algorithm especially adapted for such disordered structures. We apply it to a system of silicon dots embedded in silicon dioxide.

II. PHYSICS AND NUMERICS

A. Physics

Electronic states in the isotropic effective mass approximation [2] and charging energies [3] are calculated separately for each nanocrystal. Electron transfer is calculated in the frame of Marcus theory [4]. This theory includes both electron-phonon interactions inside each nanocrystal, and the polarization field response of the dielectric environment. Fig. 1 illustrates the importance of correctly taking into account these interactions, by their effects on position and width of resonance peak. Following this theory, the inelastic transfer rate Γ_{ij} between localized states i and j is given by the Marcus formula:

$$\Gamma_{ij} = \frac{2\pi}{\hbar}\left|H_{ij}\right|^2 \frac{1}{\sqrt{4\pi\lambda_{ab}k_{\mathrm{B}}T}} \exp\left(-\frac{\left(\lambda_{ab}+\Delta E_{ij}\right)^2}{4\lambda_{ab}k_{\mathrm{B}}T}\right) \quad (1)$$

The total rate for one carrier to tunnel from a nanocrystal a to b is the sum over the probability to tunnel from any localized state on the nanocrystal a to any localized state on b:

$$\Gamma_{ab} = \sum_{ij} f_i g_i g_j \Gamma_{ij} \quad (2)$$

f_i is the Fermi-Dirac occupation probability of the state i calculated for one electron inside the nanocrystal a and g_i (g_j) is the degeneracy of the state i (j).

λ_{ab} is the total reorganization energy associated with electron tunnelling given by:

$$\lambda_{ab} = \lambda_a^{\mathrm{in}} + \lambda_b^{\mathrm{in}} + \lambda_{ab}^{\mathrm{out}} \quad (3)$$

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The first two terms characterize the electron-phonon coupling inside both nanocrystals. We have employed the constant value λ^{in} = 12 meV [4]. The last term accounts for the polarization field response of the dielectric environment. It is given by:

$$\lambda_{ab}^{out} = \frac{q^2}{4\pi\varepsilon_0}\left(\frac{1}{2R_a}+\frac{1}{2R_b}-\frac{1}{d_{ab}}\right)\left(\frac{1}{n_{matrix}^2}-\frac{1}{\varepsilon_{matrix}}\right) \quad (4)$$

where R_a and R_b are the radii of the nanocrystals *a* and *b* respectively, d_{ab} is the center-to-center distance between the nanocrystals *a* and *b*. The refractive index is n_{matrix} = 1.46 and the static dielectric constant ε_{matrix} = 3.8 for SiO_2 where n^2 is the dynamical dielectric constant.

H_{ij} is the weak electronic coupling given by the Bardeen formula [5]:

$$H_{ij} = \frac{\hbar^2}{2m_{out}^*}\iint\left(\Psi_i\vec{\nabla}\Psi_j - \Psi_j\vec{\nabla}\Psi_i\right)d\vec{S} \quad (5)$$

where *S* is a surface lying between the nanocrystals and Ψ_i (Ψ_j) is the electronic wave functions of the state *i* (*j*). As the crystalline orientation of the nanocrystals is assumed to be distributed randomly, the wave functions Ψ are replaced by $R/(4\pi)^{1/2}$, where R is the radial part of the envelope function.

ΔE_{ij} is the energy difference experienced by a carrier tunnelling from one nanocrystal to another. It is the sum of three terms:

$$\Delta E_{ij} = \Delta E_{ij}^0 + \Delta E_{ab}^F + \Delta E_{ab}^C \quad (6)$$

ΔE_{ij}^0 corresponds to the energy levels difference and includes the quantum confinement effect. ΔE_{ab}^F is related to the applied electric field F_{ext} along the direction z:

$$\Delta E_{ab}^F = qF_{ext}\left(z_b - z_a\right) \quad (7)$$

ΔE_{ab}^C is the change in the self-interactions:

$$\Delta E_{ab}^C = \Sigma_b - \Sigma_a \quad (8)$$

where Σ is the self-energy arising from the interaction between the charge and its own image charge at the nanocrystal interface [3].

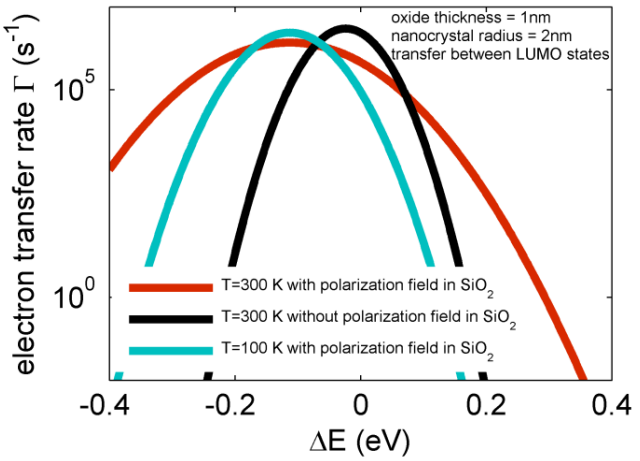

Figure 1. Electron transfer probability per unit time as a function of the energy difference ΔE.

B. *Numerics*

The basis of our numerical method is a Kinetic Monte Carlo algorithm (KMC). But, to address the complexity of an arbitrary degree of disorder specific of each nanocrystal fabrication, it is mandatory to overcome a major limitation of the standard KMC method.

Indeed, as soon as disorder is introduced, the time scale between rare and frequent events becomes large due to the exponential dependence of the tunnelling rates $\{\Gamma_{ab}\}$ with the oxide thickness between adjacent nanocrystals. Accordingly, electrons hop many times among a couple of nanocrystals without participating to the global conduction of the system. This results in an intractable consumption of CPU time.

To circumvent such problem, we have chosen to adapt a recently published method, the Accelerated Superbasin Kinetic Monte Carlo (ASKMC) method [6] to our problem. The flowchart of the algorithm is given in Fig. 2.

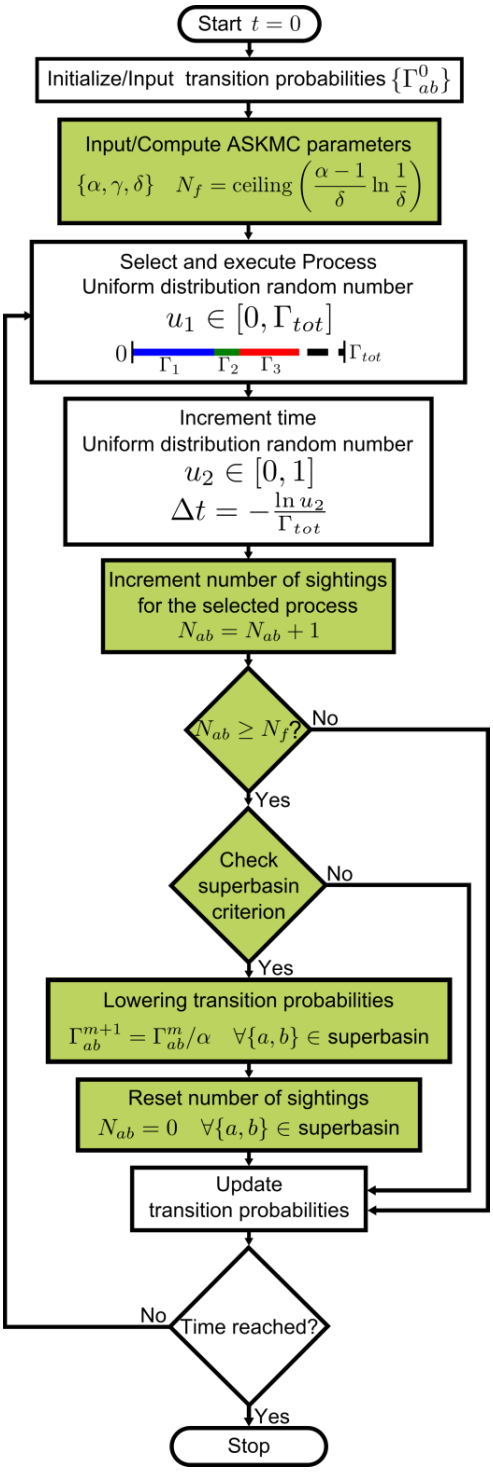

Figure 2. Flowchart of the KMC algorithm (white blocks only) and the ASKMC algorithm (both white and green blocks). The superscript *m* refers to the number of times the transition probability has been lowered.

The principle of this method is the following: it adaptively detects the groups of nanocrystals, called SuperBasins (SB), where useless events occur, and then it provides acceleration by gradually lowering the rate constants observed many times during the simulation. As a consequence, fast processes are slowed down and slow processes are executed more often.

Actually, within a SB where numerous electron transfers occur, a local equilibrium is achieved before the electron escapes from it. The ASKMC method is designed to maintain this equilibrium while lowering the transition rates belonging to the SB. In this way the error remains reasonable. The numerical parameters of the method are tuned to address the specificity of the physical problem. We have employed $\alpha = 1.5$, $\gamma = 2$ and $\delta = 0.1$.

III. RESULTS

Our test structure is a solid of silicon nanocrystals embedded in silicon dioxide. The nanocrystals are placed on a $3 \times 3 \times 3$ cubic lattice with periodic boundary conditions. Every calculation is repeated until good statistical convergence is reached.

Fig. 3 shows the electron mobility as a function of the electric field for several temperatures. The oscillations are due to the relative positions of energy levels in the nanocrystals. And, as expected, the oscillation amplitude decreases with increasing temperature, due to the broadening of energy levels plotted in Fig. 1.

Fig. 4 shows that electron mobility is weakly impacted by size disorder at room temperature, which is consistent with recent experimental results performed on PbSe nanocrystal solids [7]. It also shows that the slope of the curve, mobility versus 1/T, depends on disorder. However, when oxide thickness is not artificially fixed to a single value between adjacent nanocrystals whatever the size disorder, percolation paths compensate the effect of disorder. In the absence of disorder, the mobility still depends on the temperature because of the reorganization energy λ. Moreover, this temperature dependence may be changed by the applied electric field (Fig. 3). All of this may question about too simple interpretations of experimental data found in literature.

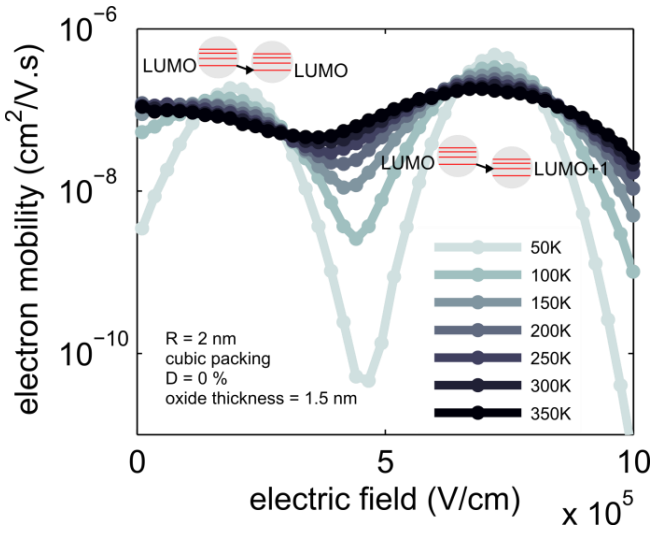

Figure 3. Electron mobility as a function of the electric field.

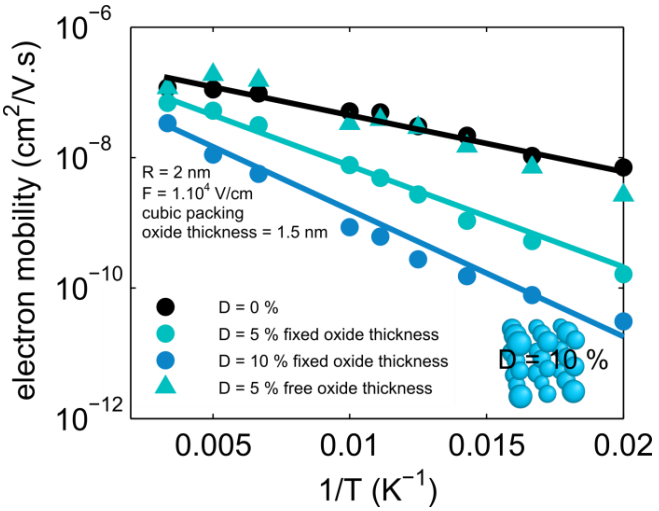

Figure 4. Electron mobility as a function of the inverse temperature. Nanocrystal sizes are randomly drawn from a log-normal distribution. D is the relative size dispersion.

IV. Conclusion

This paper presents a general method to numerically describe hopping transport through nanocrystal solids. It provides insight onto the factors impacting the mobility to prevent from misinterpretation. In particular, for silicon nanocrystals embedded in SiO_2, size disorder induces rather weak reduction of mobility at room temperature as observed by Liu *et al.* for PbSe nanocrystals [7]. Furthermore, the results suggest that experimental conductivity as a function of temperature is not sufficient to discriminate the influence of disorder. Finally, this paper provides quantitative results about the electron mobility in silicon nanocrystals embedded in SiO_2 which could be useful inputs to estimate the potential applications.

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