On the Simulation of Single Electron Transport in a Strongly Disordered Medium

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Abstract

Mesoscopic simulations of electron transport in disordered materials are based on the many particle Monte-Carlo (MC) methods. One of the major disadvantages of the multi-electron MC modeling is that the simulation process becomes significantly slow as the concentration of electrons increases. This problem makes it almost impossible to gain information about the electron transport at high Fermi levels. Recently a single-particle MC model has been proposed which is based on the truncated density of localized states (DLOS) and benefits from very short time execution. Although this model can successfully clarify the properties of the electron transport in moderately disordered systems (e.g. nanocrystalline TiO₂), utilizing the single-particle MC model for a strongly disordered medium (e.g. nanocrystalline ZnO) may conduct erroneous estimation of the electron transport coefficient. The limitation of this single-particle MC model originates primarily from using a truncated DLOS. Another obstacle of the model is that it ignores the spatial occupation of localized states in the transport medium. In this regard, for a strongly disordered medium, the deviation of the single-particle MC model is quite large when compared with theoretical the predictions. Here, based on the modified electron residence time in the localized states, we propose a different single-particle MC model which covers the aforementioned models’ drawbacks and simultaneously reduces the simulation time. The proposed model is justified by theoretical calculations for a simple cubic lattice at wide range values of disorder parameter, Fermi level, and temperature.
I. INTRODUCTION

Inorganic nanocrystalline and microcrystalline metal oxide materials such as $\text{TiO}_2$ and $\text{ZnO}$ have been drawing a lot of attention due to their photovoltaic and photocatalytic applications.\cite{1,2} In the most of these applications electron transport plays a key role in the overall performance of the device. Therefore, description and modeling of the electron transport in these materials are very important. Because of structural disorder, the electronic states in these materials are localized and the density of localized states (DOLS) is given by\cite{3,4}

$$g(E) = \frac{N_t}{kT} \exp\left(\alpha \frac{E}{kT}\right)$$

where $k$ is the Boltzmann constant, $\alpha$ is energy disorder parameter and is related to the characteristic temperature of localized states as $0 < \alpha = T/T_0 < 1$.\cite{5,6} $N_t$ is total density of localized states and $E$ is energy of states with respect to a reference level (conduction band edge $E_0$ or transport level $E_l$).\cite{7,8}

Both multiple trapping (MT) and hopping models are extensively used for the description of the electron transport in disordered materials. However, the MT model appears to be more successful in the explanation of experimental observations in the field of nano-structure inorganic semiconductors.\cite{3,9,10} In the framework of MT model, it is assumed that the electron transport via extended states is slowed down by successive trapping/detrapping events induced by localized states (traps).\cite{9}

Simulation of the electron transport in such disordered media is based on the continuous-time MC random walk which offers a comprehensive approach for investigation of different morphological and energetic aspects of electrons transport.\cite{9,11,12,13,14} Almost in all cases, the effect of Fermi level position on the electron transport is considered as one of the most important parts of such investigations. For this end, two alternative approaches based on the many-particle MC simulation have been developed. In the first approach the Fermi level is considered as an input parameter of the simulation by tuning the ratio of electrons to the number of sites.\cite{9,15} In the second one, on the other hand, the Fermi level is counted as a well-defined output parameter which is calculated from the ratio of visited states to the $g(E)$.\cite{16,17} The common disadvantage of both models is the amount of time pending for the simulation execution. Depending on the values of the different simulation parameters, up to one hundred hours may be spent for a single implementation which is obviously undesirable.
Quite generally once the density of electrons is less than the total density of localized states (i.e. the electron-electron interactions can be ignored), the single-particle simulation with the benefit of short time implementation can be used. The single-particle simulation is based on the modified (truncated) DOLS which is given by\textsuperscript{17}

\begin{equation}
\label{eq:2}
g(E) = H(E - E_f) \alpha \frac{N_t}{kT} \exp(\alpha \frac{E}{kT})
\end{equation}

where $H$ is Heaviside step function (Fig. 1). This modification is relied upon the fact that for a reasonable period of time, the electron transport properties are governed chiefly by Fermi electrons.\textsuperscript{15} It was shown that the single-particle simulation can approximately reproduce many-particle results\textsuperscript{17} leading to a growing trend in the use of single-particle procedure.\textsuperscript{10,18–24} Nonetheless, utilizing this method for a strongly disordered medium may be accompanied by substantial erroneous results. There are two major sources for such drawbacks. The first one is that Eq. \ref{eq:2} is based on the zero temperature approximation where
Figure 2. The fraction of unoccupied states and the average distance between unoccupied sites as a function of Fermi level. Marks and lines represent the results of Monte-Carlo simulation and Eq. 4 respectively. $a_{0}$ is the lattice constant of simple cubic lattice.

The Fermi-Dirac distribution ($f_{FD}(E, T)$) is replaced by a step function ($f_{FD}(E, T = 0)$ see Fig. 1(b)). However, in the framework of both multiple trapping regime and hopping regime, the transport mechanism is assumed to be thermally activated (i.e. the conductance vanishes as $T \to 0$). This means that applying Eq. 2 for the thermally-activated MT or hopping transport is not self consistent. Accordingly, the truncated DLOS model is unable to predict the temperature dependency of electron transport correctly.

The second disadvantage of the single-particle MC model (Eq. 2) is that it is implicitly assumed the average distance between unoccupied states remains constant. In other words, one always deals with a spatial distribution of localized states that the average distance between unoccupied states is independent from temperature, Fermi level and disorder parameter. The density of unoccupied states can be calculated as

$$N_{imp} = \int_{-\infty}^{E_{i}=0} g(E)(1 - f_{FD}(E))dE$$

(3)
substituting \( g(E) \) from Eq. 1 and \( f_{FD} = 1/(1 + e^{(E-E_f)/kT}) \) into the above equation we obtain
\[
N_{imp} = \frac{\alpha}{1+\alpha} N_t e^{-\epsilon_f} _2F_1(1,1+\alpha,2+\alpha,-e^{-\epsilon_f})
\] (4)
where \( _2F_1 \) is the Gauss hypergeometric function and \( \epsilon_f = E_f/kT \). Assuming a homogeneous distribution of localized states, the average distance between unoccupied sites may be obtained as \( a_l = N_{imp}^{-1/3} \). Fig. 2 shows the fraction of unoccupied sites and the average distance between them with respect to the Fermi level at four different values of disorder parameter. It can be confirmed from this figure that \( a_l \) and \( N_{imp} \) are very sensitive to the position of Fermi level specially in the vicinity of reference level. In addition, it is seen that by decreasing \( \alpha \) (being more disorder) the average distance between unoccupied sites increases which signifies the region where the truncated single-particle MC model faces the challenge.

Comparing with the analytically calculations on a simple cubic lattice, we will show that these drawbacks may guide to considerably deviations in the estimation of electron transport coefficient. Our aim is to propose an alternative approach based on the modified electron residence time which is able to successfully reproduce the theoretical predictions while it benefits from fast execution.

II. SIMULATION IMPLEMENTATION

In the conventional single-particle MC random walk simulations (hereafter will be referred as model 1), at the desired Fermi level the energies of localized states are calculated according to the Eq. 2. For thermally-activated transport and in the framework of multiple trapping, the electron residence time in each trap site is given by\textsuperscript{26,27}
\[
t_i = \ln(R)\nu_0^{-1} exp\left(\frac{E_i - E_f}{kT}\right)
\] (5)
here \( \nu_0 \) is the thermal frequency\textsuperscript{28} and \( R \) is a random number uniformly distributed between 0 and 1. The simulation begins with placing an electron randomly at one of the trap sites. Then the transport time is advanced by the residence time of that site and the electron is allowed to move randomly into one the nearest neighbors. The electron transport time in the extended states is ignored in the simulation process for it is very small when compared with \( t_i \). In the thermal equilibrium the electron diffusion exhibits non-dispersive character
(i.e. after sufficiently long times)\textsuperscript{5,15,29} and the jump (tracer) diffusion coefficient can be calculated by\textsuperscript{17,30}

\[
D_J = \frac{\langle r^2(t) \rangle}{6t}
\]

where $\langle r^2(t) \rangle$ is mean-squared displacement and $t$ is total transport time.

The outlines of modified single-particle simulation (hereafter will be referred as \textit{model 2}) are as follows. The energies of trap sites are computed according to the raw DOLS Eq. 1 while the electron residence time is modified as

\[
    t_i = (1 - F_i) \ln(R) n_0^{-1} \exp\left(\frac{E_i - E_f}{kT}\right) + \tau
\]

In this equation $\tau$ is relaxation time constant for elastic scatterings in delocalized states and orders of magnitude smaller than the inverse of thermal frequency.\textsuperscript{14,31} $F_i$ indicates the probability of occupation of the site which is calculated with respect to the Fermi-Dirac distribution

\[
    F_i = \begin{cases} 
        0 & \text{if } Rnd(0,1) > f_{FD}(E_i - E_f) \\ 
        1 & \text{if } Rnd(0,1) \leq f_{FD}(E_i - E_f)
    \end{cases}
\]

Accordingly, in the model 2, the trapping/detrapping events are taken into account only for the unoccupied states (Fig. 1). If the electron encounters with an unoccupied site, it will be trapped and both parts of the right-hand side of Eq. 7 will be counted in the total simulation time. In contrast, when the electron encounters an occupied site, it does not fall into the trap and just the value of $\tau$ will be added to the simulation time. It is noted that by this modification besides of keeping the advantage of fast implementation, the correct temperature effects, as well as the spatial occupation of traps are considered in the simulation process. The rest of simulation is similar to the model one.

Although the main advantage of MC methods is their ability for tracing the effect of different morphological aspects of the transport layer (such as roughness, porosity, and particle size) on the electron transport, here, for simplicity, we will use a simple lattice of trap sites for comparisons. All of the simulations were carried out in a $50 \times 50 \times 50$ simple cubic lattice with a lattice constant of $a_0$. In order to reduce statistical fluctuations, the electron transport coefficient was obtained by statistical averaging over 200 runs in all of the simulations.
FIG. 3. Temporal evaluation of the electron diffusion coefficient obtained from simulations based on model 1 (indicated by m1) and model 2 (indicated by m2) at $T = 300K$ and $z = v_0 \tau = 10^{-4}$. The non-dispersive (normal) transport is defined as a region for which $dD_J/a^2 = 0$.

III. RESULTS AND DISCUSSION

Fig. 3 represents temporal evaluation of the electron diffusion coefficient for $\alpha = 0.2$ and $\alpha = 0.6$. It is seen that in the region of dispersive transport the slope of two models is identical. According to the results of model 2, for the strongly disordered medium ($\alpha = 0.2$) the normal diffusion process begins at longer times compared with model 1 (about two orders of magnitude). As it can be seen from the right panel of Fig. 3 when $\alpha$ increases (less disorder medium) the difference between two models disappears. This observation is a direct consequence of the spatial occupation of trap sites. In the framework of model 1, the electron always encounters with an unoccupied site. Consequently, the sampling rate from localized states is typically high and the thermal equilibrium with the traps is obtained at shorter times. On the other hand, in the framework of model 2 a visited trap site can be either occupied or unoccupied leading to a lower sampling rate typically smaller than the
model 1. So it is expected that the thermal equilibrium is obtained at longer times in the model 2. Since at a fixed Fermi level, the fraction of occupied states decreases by increasing $\alpha$ (Fig. 2), in the moderately disordered medium the equilibrium is obtained almost at the same time for two models.

Regardless of morphological aspects, the static electron diffusion coefficient is given by\cite{17}

\[ D_J = \frac{1}{6} \left(1 - \frac{T}{T_0}\right) \exp\left(\frac{E_f - E_l}{kT}(1 - \frac{T}{T_0})\right) \] (8)

Fig. 4 shows the electron diffusion coefficient vs. Fermi level carried out at different values of $\alpha$. It is seen that at the moderately disordered medium ($\alpha = 0.6$), the results obtained from two models are identical and consistent with Eq. 8. In contrast, as the value of $\alpha$ decreases (being more disorder) the results of model 1 deviate from theoretical predictions which is more noticeable at lower Fermi levels. Similar deviations have been reported by other groups.\cite{17,18}. This deviation is due to the fact that the model 1 neglects the spatial occupation of traps as a function of Fermi level position, temperature or disorder parameter.
However, as mentioned in the introduction section the average distance between unoccupied states increases as the disorder parameter of the system rises. In addition, the model 1 always overestimates the electron diffusion coefficient. The reason is that when the Fermi-Dirac distribution is replaced by a step function, the unoccupied deeper traps below the Fermi level are neglected and the additional occupied states above the Fermi level are considered in the trapping/detrapping events leading to average smaller residence times (see Fig. 1(b) and Eq. 5). It can be confirmed from Fig. 4 that the results of model 2 are quite consistent with the analytically Eq. 8 for the whole range of $\alpha$ and $E_f$.

Variation of the electron diffusion coefficient with respect to the temperature is depicted in Fig. 5. The Arrhenius character of both models can be verified from linear behavior of $D_j$ with respect to the inverse of the temperature. Again it is seen that as disorder (characteristic temperature of localized states, $T_0$) increases, the results of model 1 become inconsistent with the theory. This implies that at stronger disorders the model 1 predicts smaller activation energies. In comparison with model 1, for different values of $T_0$ and the whole range of $T^{-1}$ the results of model 2 retain their consistency with the Eq. 8. It is worth
FIG. 6. Diffusion coefficient as a function of cut-off radius (total number of accessible sites) at different Fermi levels. The values of $\gamma_1$ and $\gamma_2$ obtained by nonlinear curve fitting tools of ORIGIN, noting that due to the exponential dependence of residence time on the temperature (Eq. 5 and Eq. 7), two models converge as temperature rises.

The simulations presented in Fig. 3 – Fig. 5 are based on the nearest neighbor movement for which $r_{cut} = a_{l0}$. Since the multiple trapping model does not depend on the distance between localized states, the zone of possible target sites can be arbitrary enlarged in order to reproduce practically observations. In order to investigate the effect of cut-off radius on the electron diffusion coefficient, the simulations were carried out for different values of cut-off radius and the results are summarized in Fig. 6. Assuming a power law relation $D_J \propto r_{cut}^{\gamma_1}$, it is observed that for a simple cubic lattice both models conduct to almost the same result of $\gamma_1 = 1.6 - 1.9$ (Fig. 6). This result appears to be inconsistent with $D_J \propto r_{cut}^3$ discussed elsewhere. The upper $x$ axis in the plots of Fig. 6 denotes the total number of neighbors. Utilizing a power law relation of $D_J \propto N_{neigh}^{\gamma_2}$ it was found that $\gamma_2 = 0.6 - 0.7$. Since the total number of neighbors increases as $N_{neigh} \propto r_{cut}^3$ it is expected that $\gamma_2 = \gamma_1/3$ which is observed in Fig. 6.

These results indicate that although the model of truncated DLOS is applicable for mod-
erately disordered materials like nanocrystalline $TiO_2$\textsuperscript{17,34–36}, it cannot be used for strongly disordered systems such as $ZnO$ where the $\alpha$ values are low and range between 0.05 and 0.15.\textsuperscript{37–39} The model 2, on the other hand, can be used for any disordered medium independent of the value of $\alpha$.

The proposed model can also be used for hopping transport where the transition rate between two localized states is $p_{i\rightarrow j} = \nu_0^{-1} \exp(-2r/\xi - \epsilon_{ji}/kT)$.\textsuperscript{18,40} In contrast of the MT model, in the hopping regime the distance between unoccupied states directly affects the transition probabilities which means that applying the model 1 for this regime may lead to incorrect results.

IV. CONCLUSION

In conclusion, it was shown that in the presence of strong disorder, the procedure of conventional single-particle simulation which is based on the truncated distribution of localized states may deviates considerably from theoretical predictions. The origins of the deviations were discussed on the bases of zero temperature approximation and spatial occupation of localized states. The proposed model which is based on the modified residence time (rather than modified DLOS) can reproduce successfully the analytical results for a wide range of characteristic parameters of the disordered medium. Eventually, it should be emphasized that the truncated DOLS model is quite applicable to moderate disorders.

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1 Y. Bai, I. Mora-Sero, F. De Angelis, J. Bisquert, and P. Wang, Chemical reviews 114, 10095 (2014).
2 Y. Jin, J. Wang, B. Sun, J. C. Blakesley, and N. C. Greenham, Nano letters 8, 1649 (2008).
3 J. Nelson, S. A. Haque, D. R. Klug, and J. R. Durrant, Physical Review B 63, 205321 (2001).
4 J. Nelson, Physical Review B 59, 15374 (1999).
5. J. van de Lagemaat, K. Zhu, K. D. Benkstein, and A. J. Frank, Inorganica Chimica Acta 361, 620 (2008).
6. M. Mandoc, B. de Boer, G. Paasch, and P. Blom, Physical Review B 75, 193202 (2007).
7. I. Fishchuk, A. Kadoshchuk, A. Bhoolokam, A. d. J. de Meux, G. Pourtois, M. Gavrilyuk, A. Köhler, H. Bässler, P. Heremans, and J. Genoe, Physical Review B 93, 195204 (2016).
8. P. T. Erslev, H.-Y. Chen, J. Gao, M. C. Beard, A. J. Frank, J. van de Lagemaat, J. C. Johnson, and J. M. Luther, Physical Review B 86, 155313 (2012).
9. J. Nelson and R. E. Chandler, Coordination Chemistry Reviews 248, 1181 (2004).
10. J. Gonzalez-Vazquez, J. A. Anta, and J. Bisquert, The Journal of Physical Chemistry C 114, 8552 (2010).
11. J. Van de Lagemaat, K. D. Benkstein, and A. J. Frank, The Journal of Physical Chemistry B 105, 12433 (2001).
12. K. D. Benkstein, N. Kopidakis, J. Van de Lagemaat, and A. Frank, The Journal of Physical Chemistry B 107, 7759 (2003).
13. A. Barzykin and M. Tachiya, The Journal of Physical Chemistry B 106, 4356 (2002).
14. M. J. Cass, F. Qiu, A. B. Walker, A. Fisher, and L. Peter, The Journal of Physical Chemistry B 107, 113 (2003).
15. J. Van de Lagemaat and A. Frank, The Journal of Physical Chemistry B 105, 11194 (2001).
16. J. A. Anta, J. Nelson, and N. Quirke, Physical Review B 65, 125324 (2002).
17. J. A. Anta, I. Mora-Seró, T. Dittrich, and J. Bisquert, Physical Chemistry Chemical Physics 10, 4478 (2008).
18. J. Gonzalez-Vazquez, J. A. Anta, and J. Bisquert, Physical Chemistry Chemical Physics 11, 10359 (2009).
19. J. Gonzalez-Vazquez, V. Morales-Flórez, and J. A. Anta, The journal of physical chemistry letters 3, 386 (2012).
20. J. P. Gonzalez-Vazquez, G. Bigeriego, and J. A. Anta, Molecular Simulation 38, 1242 (2012).
21. M. Ansari-Rad, Y. Abdi, and E. Arzi, Journal of Applied Physics 112, 074319 (2012).
22. N. Abdi, Y. Abdi, E. N. Oskoee, and M. Sajedi, Journal of nanoparticle research 16, 1 (2014).
23. M. Javadi and Y. Abdi, Journal of Applied Physics 118, 064304 (2015).
24. N. Abdi, Y. Abdi, Z. Alemipour, and E. NedaeeOskoee, Solar Energy 135, 506 (2016).
25. S. Baranovski, Charge transport in disordered solids with applications in electronics, Vol. 17
(John Wiley & Sons, 2006).

26 J. van de Lagemaat, N. Kopidakis, N. R. Neale, and A. J. Frank, Physical Review B 71, 035304 (2005).

27 R. Sibatov and E. Morozova, Journal of Experimental and Theoretical Physics 120, 860 (2015).

28 M. Mesta, C. Schaefer, J. De Groot, J. Cottaar, R. Coehoorn, and P. Bobbert, Physical Review B 88, 174204 (2013).

29 R. Sibatov and V. Uchaikin, Journal of Computational Physics 293, 409 (2015).

30 M. Javadi, Y. Abdi, and E. Arzi, Solar Energy 133, 549 (2016).

31 M. Cass, A. B. Walker, D. Martinez, and L. Peter, The Journal of Physical Chemistry B 109, 5100 (2005).

32 G. Boschloo and A. Hagfeldt, The Journal of Physical Chemistry B 109, 12093 (2005).

33 J. A. Anta and V. Morales-Flórez, The Journal of Physical Chemistry C 112, 10287 (2008).

34 M. S. Alvar, M. Javadi, Y. Abdi, and E. Arzi, Journal of Applied Physics 119, 114302 (2016).

35 M. Javadi, S. Alizadeh, Y. Khosravi, and Y. Abdi, ChemPhysChem (2016).

36 M. Quintana, T. Edvinsson, A. Hagfeldt, and G. Boschloo, The Journal of Physical Chemistry C 111, 1035 (2007).

37 M. Hosni, Y. Kusumawati, S. Farhat, N. Jouini, and T. Pauporte, The Journal of Physical Chemistry C 118, 16791 (2014).

38 C. Magne, T. Moehl, M. Urien, M. Grätzel, and T. Pauporte, Journal of Materials Chemistry A 1, 2079 (2013).

39 T. Pauporté and C. Magne, Thin Solid Films 560, 20 (2014).

40 I. Fishchuk, A. Kadashchuk, S. Hoffmann, S. Athanasopoulos, J. Genoe, H. Büssler, and A. Köhler, Physical Review B 88, 125202 (2013).