Roughness-induced energetic disorder at the metal/organic interface

S.V. Novikov
A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow 119991, Russia

G.G. Malliaras
Materials Science and Engineering,
Cornell University, Ithaca, NY 14853-1501

Abstract

The amplitude of the roughness-induced energetic disorder at the metal/organic interface is calculated. It was found that for moderately rough electrodes, the correction to the electrostatic image potential at the charge location is small. For this reason, roughness-induced energetic disorder cannot noticeably affect charge carrier injection, contrary to the recent reports.

PACS numbers: 73.30.+y, 73.40.Ns
Effective injection of charge carriers is a major requirement for efficient and reliable performance of electronic organic devices (light emitting diodes, thin film transistors, and others). Understanding charge injection is intimately connected to the structure of the metal/organic interface (or the interface of an organic material with another conductive material, such as indium tin oxide), and the detailed knowledge of this structure is important for other processes and applications. Recent experimental studies indicate that the Richardson-Schottky thermionic injection

\[ j \propto \exp \left( -\frac{e\phi}{kT} + \gamma \sqrt{E} \right) \]  

(1)

is a good starting point for the description of injection process in organic devices.\(^\text{1,2,3}\) Here \( j \) is the injected current density, \( \phi \) is the height of the barrier at the interface, and \( E \) is an applied electric field. At the same time, measurements at low temperature show that the decrease of the injection current density is much smaller than the anticipated decrease according to the Richardson-Schottky model.\(^\text{4,5}\) It was suggested that the reason for this discrepancy is the effect of energetic disorder in the organic material.\(^\text{2}\) Usually, the calculation of the effect of disorder on injection is carried out using disorder parameters estimated from the charge transport data;\(^\text{4,5}\) this means that these parameters describe the disorder in the bulk of the organic material. The experimental data clearly indicates, though, that in some cases, a surface dipolar layer is formed at the metal-organic interface.\(^\text{6,7}\) It is very reasonably to assume that this layer has some degree of disorder and, hence, will provide an additional contribution to the energetic disorder at the interface.\(^\text{8,9}\)

Recently, roughness at the metal/organic interface was suggested as the source of additional energetic disorder, localized near the interface.\(^\text{9}\) A calculation of the standard deviation of the disorder \( \sigma(z_0) \) for a point charge \( e \) located at distance \( z_0 \) from the mean plane of the weakly rough metal surface having profile \( h(x, y) \) may be carried out in the following way (we assume that the mean plane of the electrode is located at \( z = 0 \)). Let us suppose that \( z_0 \ll l \), where \( l \) is the surface correlation length. Then we can consider the electrode surface at the vicinity of a charge as a flat plane and treat surface deviation \( h(x, y) \) from the mean plane as a constant. The change of the image potential at the charge location due to the shift of the surface position by \( h \) is (in the first order in \( h \))

\[ \delta \varphi(z_0) \approx -\frac{eh}{2\varepsilon z_0^2} \]  

(2)
and $\sigma(z_0)$ is estimated as

$$\sigma^2(z_0) = e^2 \langle [\delta \varphi(z_0)]^2 \rangle = \frac{e^4 h_0^2}{4\varepsilon^2 z_0^4},$$

(3)

where the angular brackets denote an average over the ensemble of realizations of the surface roughness, $h_0^2 = \langle h^2(x, y) \rangle$ is the roughness variance and $\varepsilon$ is a dielectric constant. The mean plane of the electrode is defined in such a way that $\langle h(x, y) \rangle = 0$. Eq. (3) is exactly the result of Ref. 9, though obtained in a much simpler way.

The important parameter for charge injection is the energetic disorder directly at the interface, i.e., in first several layers of organic transport molecules adjacent to the electrode. If for the very first layer $z_0 = 6 \, \text{Å}$, $h_0 = 3.5 \, \text{Å}$, and $\varepsilon = 1$, then $\sigma(z_0) = 0.7 \, \text{eV}$ (Ref. 9). Yet the validity of Eq. (3) for short distances is very dubious because of the basic assumption that organic molecules in any particular layer of organic material are situated at a constant distance $z_0$ from the mean plane of the electrode (see Fig. 1a). The size of a typical transport molecule (8-10 Å) is small in comparison to the surface correlation length (typically, $l = 20 - 50 \, \text{nm}$, Ref. 10). In this situation it is natural to expect that a better model of the interface is one where the molecules follow the electrode profile, and any particular layer is located at the constant distance $z_0$ to the actual surface of the electrode (Fig. 1b). We will see that in this model $\sigma(z_0)$ differs drastically from the estimation in Eq. (3). The calculation of $\sigma(z_0)$ along the profile of the rough metal surface is the major difference between our paper and the paper of Rahman and Maradudin, where the general expression for the mean image potential for a rough dielectric interface was obtained.

The potential for a point charge located at the vicinity of a rough metal surface obeys the Poisson equation

$$\Delta \varphi = -\frac{4\pi e}{\varepsilon} \delta (\vec{r} - \vec{r}_0)$$

(4)

with the boundary condition

$$\varphi|_{z=h(x,y)} = 0$$

(5)

We assume that the roughness is small $h_0/l \ll 1$, and Eq. (4) can be treated via a perturbation theory approach. We are going to calculate the leading contribution only. A possible approach to perform this calculation is to transform to coordinates $z_{\text{new}} = z - h(x, y)$, so for new $z$ the boundary condition is set for $z = 0$. In the new coordinates, the Poisson
equation takes the form

\[
\Delta_{\bot} \varphi + \frac{\partial^2 \varphi}{\partial z^2} \left[ \left( \frac{\partial h}{\partial x} \right)^2 + \left( \frac{\partial h}{\partial y} \right)^2 + 1 \right] - 2 \left( \frac{\partial^2 \varphi}{\partial x \partial z} \frac{\partial h}{\partial x} + \frac{\partial^2 \varphi}{\partial y \partial z} \frac{\partial h}{\partial y} \right) - \frac{\partial \varphi}{\partial z} \Delta_{\bot} h = -\frac{4\pi e}{\varepsilon} \delta (\vec{r} - \vec{z}_0),
\]

where $\Delta_{\bot}$ is a two-dimensional (2D) Laplacian and we assume $\vec{z}_0 = (0, 0, z_0)$. Note that in the new coordinates the condition $z_0 = \text{const}$ is approximately equivalent to a constant distance to the profile of the electrode (with a small correction proportional to $h_0^2/l^2$ and insignificant to our analysis).

Let us try to find a formal solution as a series

\[
\varphi = \sum_{n=0}^{\infty} \varphi_n, \quad \varphi_n \sim O(h^n), \quad \varphi_n |_{z=0} = 0,
\]

\[
\varphi_0(\vec{r}) = \frac{e}{\varepsilon |\vec{r} - \vec{z}_0|} - \frac{e}{\varepsilon |\vec{r} + \vec{z}_0|}.
\]

The first-order correction is

\[
\varphi_1(\vec{r}) = \int d\vec{r}_1 G(\vec{r}, \vec{r}_1) J(\vec{r}_1),
\]

here $G(\vec{r}, \vec{r}_1)$ is the Green function for the Laplace operator with zero boundary condition.
at \( z = 0 \), while the source term is

\[
J(\vec{r}) = 2 \left( \frac{\partial^2 \varphi_0}{\partial x \partial z} \frac{\partial h}{\partial x} + \frac{\partial^2 \varphi_0}{\partial y \partial z} \frac{\partial h}{\partial y} \right) + \frac{\partial \varphi_0}{\partial z} \Delta \perp h = -\frac{\varepsilon}{\varepsilon_0} \left[ 2 \left( \frac{\partial P}{\partial x} \frac{\partial h}{\partial x} + \frac{\partial P}{\partial y} \frac{\partial h}{\partial y} \right) + P \Delta \perp h \right] ,
\]

(9)

\[
P(\vec{r}) = \frac{1}{|\vec{r} - \vec{z}_0|} + \frac{1}{|\vec{r} + \vec{z}_0|} .
\]

Note that, in our case, the correction to \( \varphi_0 \) depends not on \( h(x, y) \) itself, but on its derivatives and vanishes for \( h(x, y) = \text{const} \), as it should be.

The Green function has the form\(^{12}\)

\[
G(\vec{r}, \vec{r}_1) = \frac{1}{4\pi^2} \int d\vec{k} e^{-i\vec{k}(\vec{r} - \vec{r}_1)} G_k(z, z_1) ,
\]

(10)

where \( \vec{k} \) and \( \vec{\rho} = (x, y) \) are 2D vectors, and the Green function \( G_k(z, z_1) \) obeys the equation

\[
\frac{d^2 G_k}{dz^2} - k^2 G_k = \delta(z - z_1) , \quad G_k(0, z_1) = 0 .
\]

(11)

The solution of Eq. (11) is

\[
G_k(z, z_1) = -\frac{1}{k} \sinh k z_+ \exp(-k z_+) ,
\]

(12)

\[
z_+ = \max(z, z_1) , \quad z_- = \min(z, z_1) .
\]

We are going to calculate the correction (8) for \( \vec{r} = \vec{z}_0 \) only, because \( \sigma^2(z_0) = \varepsilon^2 \langle \varphi_1^2(\vec{z}_0) \rangle \). A simple but lengthy calculation gives for \( \varphi_1 \)

\[
\varphi_1(\vec{z}_0) = \frac{e}{4\pi^3 \varepsilon} \int d\vec{k}_1 d\vec{k}_2 h_{\vec{k}_1 - \vec{k}_2} \exp[-(k_1 + k_2)z_0] \cosh(k_1 - k_2) z_0 - 1] ,
\]

(13)

and \( h_{\vec{k}} \) is a Fourier transform of \( h(\vec{\rho}) \). The integral (13) can be simplified further. Let us make a transition to new vector coordinates \( \vec{\rho} = (\vec{k}_1 + \vec{k}_2)/2, \vec{q} = \vec{k}_1 - \vec{k}_2 \). Then

\[
\varphi_1(\vec{z}_0) = \frac{e}{4\pi^3 \varepsilon z_0} \int d\vec{q} g(qz_0) h_{\vec{q}} ,
\]

(14)

where

\[
g(q) = \int d\vec{p} \exp(-R) \cosh Q - 1 ,
\]

(15)

\[
R = |\vec{p} + \frac{1}{2} \vec{q}| + |\vec{p} - \frac{1}{2} \vec{q}| , \quad Q = |\vec{p} + \frac{1}{2} \vec{q}| - |\vec{p} - \frac{1}{2} \vec{q}| .
\]

Function \( g(q) \) can be easily estimated for \( q \ll 1 \) and \( q \gg 1 \). In the first case we can expand the hyperbolic cosine in the integral (15) in power series of \( \vec{q} \), thus obtaining

\[
g(q) \approx \int d\vec{p} \left( \frac{\vec{p} \cdot \vec{q}}{p} \right)^2 \exp(-2p) = \frac{\pi q^2}{8} .
\]

(16)
In the opposite case \( \frac{q}{\sqrt{2}} \gg \frac{q}{1} \) analysis shows that the only significant (and equal) contributions to Eq. (15) goes from \( \vec{p} \approx \pm \frac{1}{2} \vec{q} \), so setting \( \vec{p} = \frac{1}{2} \vec{q} + \vec{s} \) we have

\[
g(q) \approx \int d\vec{s} \exp (-2s) = \frac{\pi}{2}. \tag{17}
\]

The general behavior of \( g(q) \) is shown in Fig. 2.

Finally, the variance of roughness-induced energetic disorder is

\[
\sigma^2(z_0) = e^2 \langle \varphi^2(z_0) \rangle = \frac{e^4 h_0^2}{4\pi^2 \varepsilon^2 z_0^4} \int d\vec{q} g^2(qz_0) C_{\vec{q}}. \tag{18}
\]

This equation is the major result of this paper. Here \( C_{\vec{q}} \) is the Fourier transform of the surface correlation function, which we define in a usual way (assuming spatially homogeneous roughness)

\[
\langle h(\vec{p}) h(\vec{p}_1) \rangle = h_0^2 C(\vec{p} - \vec{p}_1) \tag{19}
\]

with \( C(0) = 1 \), so \( \langle h^2(\vec{p}) \rangle = h_0^2 \). For homogeneous roughness

\[
\langle h_{\vec{k}} h_{\vec{k}_1} \rangle = 4\pi^2 h_0^2 C_{\vec{k}} \delta \left( \vec{k} + \vec{k}_1 \right). \tag{20}
\]

If \( z_0 \gg l \), then we can replace \( g(qz_0) \) by its limit value of \( \pi/2 \), and in this case

\[
\sigma^2(z_0) \approx \frac{e^4 h_0^2}{4\varepsilon^2 z_0^5}. \tag{21}
\]
This result is equivalent to Eq. (3), but it is valid only far away from the rough electrode surface. The reason for the equivalence of Eq. (21) and Eq. (3) is the need to cancel the leading term in Eq. (14) in the old (physical) coordinate system. Indeed, as it follows from Eq. (14) for $z_0 \gg l$

$$\varphi_1 (z_0) = \frac{e h}{2 \varepsilon z_0^2} + o \left( \frac{1}{z_0^2} \right) \Omega [h],$$  

(22)

where $\Omega$ is some integral operator. Image potential at the charge location is

$$- \frac{e}{2 \varepsilon z_0} + \frac{e h}{2 \varepsilon z_0^2} + o \left( \frac{1}{z_0^2} \right) \Omega [h] =$$

$$- \frac{e}{2 \varepsilon z_0^\text{old}} + o \left( \frac{1}{z_0^\text{old}} \right)^2 \Omega [h] + O(h^2)$$  

(23)

(here $z_0^\text{old}$ denotes the distance to the mean plane of the electrode). This result means that in the old (physical) coordinate system the correction to the image potential in the first order in $h$ decays faster than $1/(z_0^\text{old})^2$ for large distances. This is not surprising because this kind of decay is possible only for $h \approx \text{const}$, which is not the case for $z_0 \gg l$, where many uncorrelated domains of the rough surface contribute to the image potential.

All these intricacies are not important for charge injection, where a relevant distance to the surface of the electrode is small. If $z_0 \ll l$, then

$$\sigma^2(z_0) \approx \frac{e^4 h_0^2}{256 \pi^2 \varepsilon^2} \int d\vec{q} q^4 C_{\vec{q}} \propto \frac{e^4 h_0^2}{\varepsilon^2 l^4}.$$  

(24)

The later estimation is valid if $C(\vec{\rho})$ can be characterized by the scale $l$ only, and the integral in Eq. (24) converges for $q \to \infty$. If we assume a Gaussian correlation function

$$C(\vec{\rho}) = \exp \left( -\frac{\rho^2}{2l^2} \right)$$  

(25)

which is a good approximation for indium tin oxide electrodes\textsuperscript{10}, then for $z_0 \ll l$

$$\sigma^2(z_0) \approx \frac{e^4 h_0^2}{8 \varepsilon^2 l^4}.$$  

(26)

Eq. (26) is similar to Eq. (3) with the only crucial difference: $z_0$ is replaced by $l$. For the roughest electrode, mentioned in Ref. 10, with $h_0 = 4$ nm and $l = 14$ nm, we have at the interface $\sigma \approx 0.01$ eV.

Let us consider the case, when the integral (24) does not converge for $q \to \infty$. This is the case of the fractal rough surface with a correlation function

$$C_k = \frac{A l^2}{(1 + k^2 l^2)^{1+\alpha}}, \quad A = 4\pi \alpha \left[ 1 - \frac{1}{(1 + k^2 l^2)^\alpha} \right]^{-1},$$  

(27)
here $0 \leq \alpha < 1$ (Ref. 13). In fact, any fractal surface can be realized as an intermediate asymptotic only, for some spatial scale range, thus the proper cut-off $k_c$ is assumed in Eq. (27). For a clear physical reason (discrete nature of a real metal surface) $k_c \ll 1/a$ where $a$ is a typical interatom distance, while $k_c l \gg 1$. This means that $z_0 k_c \lesssim 1$ for the organic layers closest to the metal surface. Hence, we can still use the small-q asymptotic of $g(q)$ and

$$\sigma^2(z_0) \approx \frac{A e^4 h_0^2 l^2}{128 \pi^2} \int_0^{k_c} dq \frac{q^5}{(1+q^2 l^2)^{\alpha+1}} \approx \frac{A e^4 h_0^2 (k_c l)^{2(2-\alpha)}}{256(2-\alpha) \pi \varepsilon^4 l^4}.$$  

In the most favorable for large $\sigma$ case $\alpha \approx 0$

$$\sigma(z_0) \approx \frac{\pi e^2 h_0 k_c^2}{8 \varepsilon \sqrt{\ln(k_c l)}} \quad (29)$$

and for $h_0 = 5 \text{ Å}$ the value of $\sigma$ becomes comparable with the bulk value of 0.1 eV only for $k_c \gtrsim 0.1 \text{ Å}^{-1}$. Such value for $k_c$ seems to be unreasonably large. Scanning microscopy data indicate that typically the Gaussian correlation function (25) is a good approximation for rough electrode surfaces at nanometer scale. Fractal surfaces have been indeed observed in clusters formed by small metal particles, but the relevant spatial scale was very different: even the size of the individual metal particle was no less than 10 nm (Refs. 14, 15); in this case $k_c < 0.01 \text{ Å}^{-1}$.

In conclusion, we have found that the contribution from image forces to the roughness-induced energetic disorder is typically too weak to provide a noticeable effect on injection, contrary to the analysis in Ref. 9.

This work was supported by the ISTC grant 2207 and RFBR grants 02-03-33052 and 03-03-33067. The research described in this publication was made possible in part by Award No. RE2-2524-MO-03 of the U.S. Civilian Research & Development Foundation for the Independent States of the Former Soviet Union (CRDF).

1 J. C. Scott, J. Vac. Sci. Technol. A 21, 521 (2003).
2 V. I. Arkhipov, E. V. Emelianova, Y. H. Tak, and H. Bässler, J. Appl. Phys. 84, 848 (1998)
3 J. C. Scott and G. G. Malliaras, Chem. Phys. Lett. 299, 115 (1999).
4. T. Van Woudenbergh, P. W. M. Blom, M. C. J. M. Vissenberg, and J. N. Huilberts, Appl. Phys. Lett. 79, 1697 (2001).
5. B. H. Hamadani and D. Natelson, J. Appl. Phys. 97, 064508 (2005).
6. H. Ishii, K. Sugiyama, E. Ito, and K. Seki, Adv. Mater. 11, 605 (1999).
7. D. Cahen and A. Kahn, Adv. Mater. 15, 271 (2003).
8. M. A. Baldo and S. R. Forrest, Phys. Rev. B 64, 085201 (2001).
9. B. N. Limketkai and M. A. Baldo, Phys. Rev. B 71, 085207 (2005).
10. S.V. Novikov, Macromolecular Symp. 212, 191 (2004).
11. T.S. Rahman and A.A. Maradudin, Phys. Rev. B 21, 504 (1980).
12. S.V. Novikov and A.V. Vannikov, Synth. Metals 121, 1387 (2001).
13. Y.-P. Zhao, G.-C. Wang, T.-M. Lu, G. Palasantzas, and J. T. M. De Hosson, Phys. Rev. B 60, 9157 (1999).
14. D. P. Tsai, J. Kovacs, Z. Wang, M. Moskovits, V. M. Shalaev, J. S. Suh, and R. Botet, Phys. Rev. Lett. 72, 4149 (1994).
15. M.C. Chen, S. D. Tsai, M. R. Chen, S. Y. Ou, W.-H. Li, and K. C. Lee, Phys. Rev. B 51, 4507 (1995).