High-order calculation of triboelectric charge density using a transition matrix element in a triboelectric nanogenerator system

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Abstract
The second-order calculation for triboelectric charge density \( \sigma_{\text{tribo}} \) between a metal and polymer is performed analytically based on the molecular-ion-state model. The transition matrix element \( |M_{AB}| \) is approximately calculated for two cases where the distance between metal and polymer is very small \( (d \ll 1) \) and the electronic energy is near the Fermi energy level \( (E_F) \) because electron transfer between metal and polymer is dominant at this level. The \( \sigma_{\text{tribo}} \) approaches zero-order approximation as \( d \) approaches zero. Thus, although \( d \) is very small \( (d \ll 1) \), its effect as a second-order approximation, such as dielectric constant and dielectric thickness, is shown here.

1. Introduction

The tribo-charge density \( (\sigma) \) can be generated by contact between two triboelectric materials where, when separated as a result of \( \sigma \), an electric field \( E \) is formed between them, which can then lead to a vacuum level shift or the formation of a vacuum potential barrier \([1, 2]\). The electrons can then reach an equilibrium state by free tunneling through the barrier within the critical tunneling distance \( (4–5\, \text{Å}) \). During the equilibrium state, the initial \( \sigma \) during contact can change to the final equilibrated \( \sigma \) after separation, which is associated with the gradient of the vacuum potential barrier between the two materials. The time for tunneling through the barrier is so fast that tunneling occurs instantaneously upon reaching equilibrium. The separating distance \( (d) \) can be divided into roughly four cases: (1) if \( d \) is greater than the critical tunneling distance, then electron transfer is not allowed, reaching a non-equilibrium state; (2) if \( d \) is approximately the critical tunneling distance \((4–5\, \text{Å})\), the vacuum potential can exist between the two materials, but electron transfer is possible via quantum tunneling through the barrier; (3) if \( d \) is approximately \( 2–3\, \text{Å} \), a local potential can be formed, but it will be lower than the Fermi-energy level, so a barrier is not formed; (4) if \( d \) approaches zero, then no vacuum potential forms. This means that direct electron propagation occurs between the two materials.

Previously, zero-order calculation of the triboelectric charge density \( (\sigma) \) was performed between a metal and a polymer via the charge transfer mechanism \([3–10]\) using a transition matrix element \( |M_{AB}| \), on the condition that the separation distance is very small \( (d \ll 1) \). The \( \sigma \) can then be written as follows \([1]\):

\[
\sigma \approx \frac{2\rho_a(E_F)}{\beta A} \ln \left[ \sqrt{2} A \left( \sqrt{E_0 - \phi_m} \right) / m \right] : \text{zero - order approximation.} 
\] (1)

where \( \rho_a \) is the acceptor density of states, \( E_F \) is the Fermi-energy level, \( A \) is the interfacial area between two materials, \( \beta \) is the proportionality factor, \( E_0 \) is the work function of the polymer, \( \phi_m \) is the work function of the metal, and \( m \) is the electron mass. However, the \( |M_{AB}| \) from \( \frac{2\phi_a(E_F)}{\beta A} \ln |M_{AB}| \) can be expressed as a power series around \( d \) with \( d \ll 1 \). It then contains \( \sigma \) with higher orders. Therefore, solving \( \sigma \) equations with high orders can approach a more realistic value, in principle. In this paper, the second-order triboelectric charge density is calculated by solving a 'quadratic' equation of \( \sigma \) including a structural parameter and material parameter.
2. High-order calculation of \( \sigma_{\text{tribo}} \) using \(|M_{AB}|\) (transition matrix element)

Previously, the triboelectric charge density was derived using a transition matrix element \(|M_{AB}|\) between a metal and a polymer whose acceptor density of states is assumed to be known as \( \rho_A(E_F) \) at the Fermi-energy level \( E_F \).

The tribo-charge \( Q \) can be expressed as

\[
Q = -q \cdot \rho_A(E_F) \cdot \Delta E
\]

\[
= -q \cdot \rho_A(E_F) \cdot \left\{ \ln[k'] - \frac{2 \ln |M_{AB}|}{\beta} \right\}
\]

\[
= \frac{-q \cdot \rho_A(E_F) \cdot \ln[k']}{\beta} + \frac{2q \cdot \rho_A(E_F) \cdot \ln |M_{AB}|}{\beta}.
\]

(2)

where \( \Delta E \) is the energy difference of the Fermi-energy level, \( q \) is the elementary charge, and \( k' \) is the proportionality factor. Thus, tribo-charge density can be written as

\[
\frac{Q}{A} = \sigma = \frac{-q \rho_A(E_F) \ln[k']}{\beta A} + \frac{2q \rho_A(E_F) \ln |M_{AB}|}{\beta A}.
\]

(3)

If the separation distance \( d \) is very small, then \( \ln |M_{AB}| \) can be written as a power series around \( d \) at an energy near \( E_F \).

\[
\ln |M_{AB}| = \ln \left[ \sqrt{2} A \sqrt{\frac{E_0 - \phi_m}{m}} - \frac{q \sigma d}{2E_0\varepsilon_0 - 2\varepsilon_0\phi_m} + \frac{2q\sigma(E_F - \phi_m)}{\varepsilon_0} + \frac{E_0^2m(\phi_m - E_F)}{\hbar^2} \right]^2 + O[d^3].
\]

(4)

where \( \varepsilon_0 \) is the vacuum permittivity, \( \varepsilon \) is the dielectric constant, \( t \) is the dielectric thickness, and \( \hbar \) is the reduced plank constant.

More specifically, the zeroth order calculation of \( \sigma \) can be rewritten as

\[
\frac{Q}{A} = \sigma = \frac{-q \rho_A(E_F) \ln[k']}{\beta A} + \frac{2q \rho_A(E_F) \ln |M_{AB}|}{\beta A}.
\]

(5)

where some constant of \( -\frac{q \rho_A(E_F) \ln[k']}{\beta A} \) is added to equation \( 1 \).

2.1. First-order approximation

The first-order calculation of \( \sigma \) can be obtained in the following manner:

\[
\sigma \approx \frac{-q \rho_A(E_F) \ln[k']}{\beta A} + \frac{2q \rho_A(E_F) \ln \left[ \sqrt{2} A \sqrt{\frac{E_0 - \phi_m}{m}} - \frac{q \sigma d}{2E_0\varepsilon_0 - 2\varepsilon_0\phi_m} \right]}{\beta A}.
\]

(6)

The first term in equation \( 6 \) is a constant, and the second term comes from the matrix element \( |M_{AB}| \). By solving equation \( 6 \) for \( \sigma \), this \( \sigma \) can be approximately calculated as follows:

\[
\sigma \approx \frac{q \varepsilon_0 \rho_A(E_F)(E_0 - \phi_m) \left[ \ln[2] - \ln[k'] + 2 \ln \left[ A \sqrt{\frac{E_0 - \phi_m}{m}} \right] \right]}{dq^2 \rho_A(E_F) + A\beta \varepsilon_0(E_0 - \phi_m)}.
\]

(7)

If \( d \) approaches zero, then \( \sigma \) will be reduced to the previous result (zeroth order) \([1]\).

The first-order \( \sigma \) in equation \( 7 \) can also be stated as follows using a power series expansion around \( d \).

\[
\sigma \approx \sigma (\text{zeroth order}) + \Delta_1.
\]

(8)

\[
\Delta_1 = \frac{dq^2 \left( -2 \ln \left[ A \sqrt{\frac{E_0 - \phi_m}{m}} \right] + \ln \left[ \frac{k'}{2} \right] \right) \rho_A(E_F)^2}{A \beta (dq^2 \rho_A(E_F) + A\beta \varepsilon_0(E_0 - \phi_m))}.
\]

(9)

where \( \Delta_1 \) indicates the difference between the first-order and zero-order \( \sigma \).

2.2. Second-order approximation

The second-order calculation of \( \sigma \) can be obtained in a manner similar to that used for equation \( 6 \), but the \( d^2 \) term is added.
This implies that it is a tunneling duration per transition probability.

Figure 1 shows a band diagram where charges are transferred from a metal to a polymer through an energy window, $\Delta E$, which is related to the transition matrix element $|M_{AB}|$ where $|M_{AB}|^2 = k' e^{-\Delta E/\beta}$. The square of $|M_{AB}|$ is exponentially decaying as $\Delta E$ increases. That is, the probability of electron transfer is reduced as the energy difference of $E_p$ increases. $k'$ and $\beta$ are proportionality factors.
To be more precise, the second-order calculation of the triboelectric charges ($\sigma$) is performed in this work. Because, $|M_{AB}|$ contains $\sigma$ with $d^2$ terms as shown in equation (10). The filled states of the lowest unoccupied molecular orbital (LUMO) energy level transferred from the electrons in the metal at the Fermi-energy level is shown in figure 1, aligning with the Fermi-energy level when equilibrium states reach.

The unit of polymer acceptor density of states $r_{EA}$ is the number of states per eV at the surface, which can be obtained from the experimental bulk acceptor density of states if it is uniform. Then, the induced tribo-charges can be obtained from the polymer acceptor density of states (DOS) at the surface, as they are surface charges.

Figure 2 shows a plot of second-order calculation of $\sigma$ as a function of dielectric constant ($\varepsilon$) and dielectric thickness ($t$). Among the two solutions obtained, only one solution has a physical meaning. The parameters used to plot are as follows: $E_0 = 4$[eV], $\phi_m = 1$[eV], $\hbar = 1.054 \times 10^{-34}$ [J $\cdot$ s], $k' = 2$, $\rho_A = 10^3[1/J]$, $\beta = 10^{19}$, $A = 1[cm^2]$, $m = 9.11 \times 10^{-31}[kg]$, $\varepsilon_0 = 8.854 \times 10^{-12}[F/m]$, $d = 4[\AA]$, and $q = 1.6 \times 10^{-19}[C]$. In the plot, as $t$ increases, $\sigma$ decreases; and as $\varepsilon$ increases, $\sigma$ also increases. From a mathematical point of view, the following term is contained in the second solution in equation (12).

$$
\sigma \sim \frac{\varepsilon_0(E_0 - \phi_m)}{d^2 q^2 t \rho_A(E_F)} \{d \cdot q^2 d \cdot \varepsilon \cdot \rho_A(E_F) \}
\sim \frac{\varepsilon_0(E_0 - \phi_m)\varepsilon}{q \cdot t} \sim \frac{\varepsilon}{t}.
$$

This implies that $\sigma$ is proportional to $\varepsilon$ and inversely proportional to $t$. This is also expected when calculating the second-order $\sigma$ using $\ln |M_{AB}|$, which includes only a term of $\varepsilon$ and $t$. 

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**Figure 1.** A schematic band diagram for the metal-to-polymer tribo-nanosystem. $\Delta E = \text{window associated with } |M_{AB}|.$

**Figure 2.** 3D plot of second-order $\sigma$ as a function of dielectric constant ($\varepsilon$) and dielectric thickness ($t$).
The calculated second-order $\sigma$ from equation (12) can be asymptotically approximated as follows for $E_0 - \phi_m \gg 1$.

$$\sigma \approx \frac{q \cdot t \cdot \varepsilon_0 \rho_A(E_F)(E_0 - \phi_m)}{d \cdot q^2(t - d \cdot \varepsilon)\rho_A(E_F) + At\beta\varepsilon_0(E_0 - \phi_m)} \left\{ \ln[2] - \ln[k'] + 2\ln \left[ A \cdot \sqrt{\frac{E_0 - \phi_m}{m}} \right] \right\}.$$  

(20)

This indicates that $\sigma$ is proportional to $-\ln[E_0 - \phi_m]$, with $\rho_A(E_F)$ shown in figure 4.

4. Conclusion

The $\sigma_{\text{tribo}}$ (transferred tribo-charge density from metal to polymer) is calculated based on the molecular-ion-state model. Here, the transition matrix element used is power expanded about $d$ until $d^2$ to calculate the second-order $\sigma_{\text{tribo}}$. The $d$ is the charge-transfer interface distance between metal and polymer within the critical
tunneling distance. It is assumed that the charge transfer occurs at the Fermi-energy level, which is the dominant electronic energy state. The second-order \( \sigma_{\text{tribo}} \) should be calculated to reflect the dielectric constant \( (\varepsilon) \) and dielectric thickness \( (t) \) on \( \sigma_{\text{tribo}} \). This mathematical result leads back to a previous result [1] where \( d \) is zero.

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