Understandabe Approach about Electric and Dielectric Properties of Conductive Filler-Polymer Composites in terms of Elementary Quantum Mechanics

Masaru Matsuo

Co-authors Rong Zhang, Yuezhen Bin,

Department of polymer science and material, Dalian university of technology, Dalian 116024, People's Republic of China

Polychar 26 Tbilisi, Georgia, October 10-13th

#### **Two Discussion Points in terms of Educational Aspect**

[1] Conductivity of Polymer-conductive (semi-conductive) fillers increases with elevating temperature up to glass temperature. This is attributed to an increase in electron tunneling. This analysis has been pursued by very simplified equation proposed by Scheng. However, the distance between conductive fillers is picometre size indicating out of framework of polymer science. On the other hand, the distance calculated by the original equation is reasonable nano scale. However, his original equation is very difficult and this talk shall make a commentary on the concept of the equation. Before the commentary, the history of electron tunneling, the history of electron tunneling mainly evaluated at absolute temperature in terms of simple quantum mechanics.



[2] The tunneling current is direct current (DC). This value can not be related to the morphology of the system, since the resistivity of the system was reflected by three:

- 1) the interference resistance between electrode and composite,
- 2) resistance of the grain boundary region between filler and polymer 3) filler resistance.

To classify them, curve fittings between experimental complex impedance and that calculated by three-unit model and three kinds of resistivity was determined at frequency = 0 (DC component) and the distance between adjacent fillers was determined.



The method and system for detecting leakage in electronic device are important, because of recent miniaturization of semiconductor device.

The leakage current generates through thinned insulator film by tunneling electrons associated quantum mechanics.



Surfaces of Cu wire are coated by very thin oxide film with insulation property. Even so, the connected Cu wire pass through current smoothly.

Current mechanisms of polymer-filler systems have been discussed by SEM simply in terms of the observation of continuous filler ensuring electric channels. The surface of Cu wires are coated by oxide film with insulation property. Even so, current pass through the connected Cu wire smoothly. The positive temperature coefficient (PTC) effect by polymer-conductive (semi-conductive) composite have been applied to floor heating and electro-thermal wear materials. The electron tunneling mechanism is discussed in relation to the morphology of the system by complex impedance. Some references in our group are as follows:

Polymer Journal 49, 839-850 (2017) Macromolecules 47(3) 8281-8294 (2014) J. Phys. Chem. B. 118, 7047-7058 (2014) Polymer 55, 2597-2608 (2014) J. Phys. Chem. B. 2014, 118, 2226-2237 *Polymer Journal* 45, 1120-1134 (2013) *Polymer* 53 5197-5207 (2012) J. Phys. Chem. A 116(9) 2024-2031 (2012) Langmuir, 26 (4), pp 2857–2863 (2010) J. Polymer Sci. Part B 47(13) 1253-1266 (2009) Carbon 47, 1311-1320 (2009) Polymer 50, 1046-1053 (2009) Phys.Rev. B 77(3), 035419 (2008)



Figure. Temperature dependence of resistivity for PE/carbon black (CB), PE/carbon fiber (CF) and PE/carbon nanotube (CNT)

To avoid PTC effect, polyimide (PI) is used as matrix to deduce an increase in electron tunneling with elevating temperature, since PI is very few thermal expansion at temperature up to 160°C.



The lectures about detailed electron tunneling for graduate and undergraduate students studying polymer science are not in detail and the teaching staffs are not very knowledgeable about the electron tunneling.

This talk is focused on easy-to-understand explanation of electron tunneling.

#### Focus on the present talk

VGCF (vapor-grown carbon fiber) : Rigid semi-conductive filler PI : rigid amorphous polymer with a very low thermal expansion

Very low thermal expansion is important to verify that an increase in conductivity with increasing temperature is attributed to active electron transfer between adjacent VGCF surfaces (tunneling current), since the gap distance (*D*) between adjacent VGCFs may be postulated to be constant and independent of external heating temperature.



The present section deals with Schrödinger's wave function in a way concerning basic knowledge of physics at the high school level. Generally, wave function is represented as a trigonometric function. Traveling wave to right with velocity *u* moves *ut* in the *x* direction (one dimensional case) after time *t* as shown in the lower Fig.



**Travelling wave** 

 $\Psi$  is one of the solution of the following differential equation.

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{u^2} \frac{\partial^2 \Psi}{\partial t^2} \qquad \Psi = A \cos 2\pi (kx - vt)$$

 $\Psi = A\cos 2\pi (kx - vt) + i\sin 2\pi (kx - vt) = A\exp[2\pi i(kx - vt)]$ 

$$\Psi = A\cos 2\pi (kx - vt) + i\sin 2\pi (kx - vt) = A\exp[2\pi i(kx - vt)]$$

The above Eq. can be applied to de Broglie wave representation as a wave but it is independent of wave-particle duality.

To combine the relationship between particle and wave properties, the following replacement must be emphasized:

$$E = h \nu \qquad k = \frac{1}{\lambda} = \frac{p}{h} \qquad (\lambda = h/mv = h/p) \qquad \begin{array}{l} h : \text{Planck's constant} \\ p : \text{momentum} \end{array}$$
$$\Psi = A \exp\left[\frac{2\pi i}{h}(px - Et)\right] \qquad (1)$$

Eq. (1) contains both properties of particles and waves. The differentiation with respect to *x* gives as

$$\frac{\partial \Psi}{\partial x} = \frac{2\pi i}{h} p \Psi \qquad p \Psi = \frac{h}{2\pi i} \frac{\partial}{\partial x} \Psi$$

By differentiating Eq. (1) with respect to *t*,

$$E = -\frac{h}{2\pi i}\frac{\partial}{\partial t}\Psi$$

Given the difficulties already noted, the instructor needs to emphasize that Schrödinger's wave function is an equation formulated only by replacement of E = hv,  $k = 1/\lambda = p/h$  ( $\lambda = h/mv = h/p$ ) - as discussed before. To pursue this approach, we now consider an example for kinetic energy:

$$\frac{1}{2}m\,v^{2} = \frac{1}{2m}(mv)^{2} = \frac{p^{2}}{2m}$$

When considering potential energy V, total energy E in one dimension is given by

$$E = \frac{1}{2}mv^2 + V = \frac{1}{2m}p^2 + V$$

In one-dimension,

$$\frac{1}{2m}p_x^2 + V(x) = E$$

$$p\Psi(x,t) = \frac{h}{2\pi i} \frac{\partial}{\partial x} \Psi(x,t) \qquad E = -\frac{h}{2\pi i} \frac{\partial}{\partial t} \Psi(x,t)$$

 $\left[\frac{1}{2m}\left(\frac{h}{2\pi i}\right)^2 \left(\frac{\partial^2}{\partial x^2}\right) + V(x)\right] \Psi(x,t) = -\frac{h}{2\pi i}\frac{\partial}{\partial t}\Psi(x,t) \qquad \text{Rearranging this equation,}$ 

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} - \frac{8\pi^2 m}{h^2} V(x) \Psi(x,t) + \frac{4\pi m i}{h} \frac{\partial \Psi(x,t)}{\partial t} = 0$$

**By variable separation of**  $\Psi(x,t)$ ,  $\Psi(x,t) = \varphi(x)g(t) = \varphi g(t)$ 

$$\frac{1}{\varphi} \left\{ \frac{\partial^2 \varphi}{\partial x^2} - \frac{8\pi^2 m}{h^2} V \varphi \right\} = -\frac{4\pi m i}{h} \frac{1}{g(t)} \frac{dg(t)}{dt}$$

The left side of the above Eq. is given as a function of *x*, while the right side as a function of *t*. Hence the value of the above Eq. must be constant and can be represented by  $8\pi^2 mE/h^2$ ;

Here *E* is a arbitrary constant at present but will be shown to stand for the total energy later. The left and right sides may be represented by

$$\frac{\partial^2 \varphi(x)}{\partial x^2} + \frac{8\pi^2 m}{h^2} (E - V) \varphi(x) = 0 \quad (1)$$

$$\frac{dg(t)}{dt} = -\frac{2\pi i}{h} Eg(t) \quad \Rightarrow \quad g(t) = g_o \exp\left(-2\pi i \frac{E}{h}t\right) \quad g_o \text{ is constant.}$$

Eq. (1) relating to the position (x) has been known as Schrödinger's wave function. The instructor has to emphasize that de Broglie wave is a travelling wave; since the electron is locked in a very small volume like that of an atom, the corresponding de Broglie wave can be treated as a standing wave whose amplitude depends on a function of position. The significance of this approach shall be described later. Let's consider the system that an electron with V = 0 is confined in the cliff valley of potential  $(V = \infty)$  as shown in Fig. (a). For very simple analysis, the electron cannot exist at x < 0 and x > a, because of  $V = \infty$  and  $\varphi = 0$ . On the other hand, V = 0 is satisfied at 0 < x < a and Schrödinger's wave function becomes as follows:

$$\frac{\partial^2 \varphi}{\partial x^2} + \frac{8\pi^2 m}{h^2} E\varphi = 0$$

The solution is given by

$$\varphi_n = \sqrt{\frac{2}{a}} \sin \frac{n \pi x}{a} \ n = 1, 2, 3, \dots$$

On the calculation process, *E* is induced as

$$En = \frac{n^2 h^2}{8ma^2}$$

The result is shown in Fig. (b).



As shown in Fig. (c), however, the thickness $\delta$  of the cliff valley with finite height  $V_L$  is very thin, the electron can pass through the potential barrier (the cliff valley). The phenomenon is termed as tunnel effect and the possibility of the electron tunneling is proportional to

$$\exp\left(-\frac{4\pi\delta}{h}\sqrt{2m(V_L-E)}\right) \qquad \qquad \mathbf{WKB approximation}$$

 $\mathcal{E}_F$ :

The possibility is surely related to tunnel current but the actual equation representing tunnel current density must be derived by much complicated process using WKB approximation. The above possibility can be constructed when the potential barrieris flat independent of  $\delta$ .



 $\mathcal{E}_F$ : Fermi-Dirac energy

The energy level of tunneling electrons is lower than Fermi-Dirac energy. The above possibility can be constructed when the potential barrier is flat. The well-known tunnel current is derived for the arbitrary shape V(x).

In this case, the permeability coefficient  $D(E_x)$  in the *x* direction calculated by WKB approximation is given by

$$D_x \approx \exp\left(-\frac{4\pi}{h}\int_a^b \sqrt{2m(V(x)-E_x)}dx\right)$$

The density J of electron current is given by

$$J = eN = \int_0^{E_m} D(E_x) dE_x \left\{ \frac{4\pi m^2 e}{h^3} \int_0^\infty \left[ f(E) - f(E + eV) \right] dE_r \right\} = \int_0^{E_m} D(E_x) \zeta dE_x$$

Fermi-Dirac distribution function f(E)

a





 $\mu$  : chemical potential

### **Classical representation for tunneling current by Simmons**

A very insulating and very thin film is set between two electrodes, current can flow by means of tunneling effect. Many papers have been reported. This paper introduced the tunneling current reported by Simmons. The diagram is similar to Simmons. [Simmons, J. Appl. Phys. 34, 1793, (1963)]



 $E_x$  is the energy component of the incident electron in the x direction.

The net flow of electrons  $N (= N_1 - N_2)$  through the barrier is

$$N = \int_{0}^{E_{m}} D(E_{x}) dE_{x} \left\{ \frac{4\pi n^{2}}{h^{3}} \int_{0}^{\infty} \left[ f(E) - f(E + eV) \right] dE_{r} \right\}$$

Accordingly, tunnel current density J is written by using charge electron e.

$$J = eN = \int_{0}^{E_{m}} D(E_{x}) dE_{x} \left\{ \frac{4\pi m^{2} e}{h^{3}} \int_{0}^{\infty} [f(E) - f(E + eV)] dE_{r} \right\} = \int_{0}^{E_{m}} D(E_{x}) \zeta dE_{x}$$
$$\zeta = \zeta_{1} - \zeta_{2} \qquad \zeta_{1} = \frac{4\pi m^{2} e}{h^{3}} \int_{0}^{\infty} f(E) dE_{r} \qquad \zeta_{2} = \frac{4\pi m^{2} e}{h^{3}} \int_{0}^{\infty} f(E + eV) dE_{r}$$

The above Eq. is the general equation to represent tunnel current density. Let's consider current-voltage relationship. To pursue the analysis, the potential barrier height V(x) is represented as  $V(x) = \eta + \phi(x)$ . Thus

$$D(E_x) = \exp\left[-\frac{4\pi}{h}(2m)^{1/2}\int_a^b (\eta + \phi(x) - E_x)^{1/2} dx\right]$$
  
By very nice approximation by Simmons,  $D(E_x) \approx \exp\left[-A(\eta + \overline{\phi} - E_x)^{1/2}\right]$ 

 $\overline{\phi}$  is the means barrier height above Fermi level of the negatively biased electrode and is given by

1 .h

$$A \approx \frac{4\pi d}{h} (2m)^{1/2}$$

$$\overline{\phi} = \frac{1}{d} \int_{a}^{b} \phi(x) dx \qquad s_1 \rightarrow a, \qquad s_2 \rightarrow b$$

The net flow of electrons  $N (= N_1 - N_2)$  through the barrier is

$$N = \int_{0}^{E_{m}} D(E_{x}) dE_{x} \left\{ \frac{4\pi m^{2}}{h^{3}} \int_{0}^{\infty} \left[ f(E) - f(E + eV) \right] dE_{r} \right\}$$

Accordingly, tunnel current density J is written by using charge electron e.

$$J = eN = \int_{0}^{E_{m}} D(E_{x}) dE_{x} \left\{ \frac{4\pi m^{2} e}{h^{3}} \int_{0}^{\infty} [f(E) - f(E + eV)] dE_{r} \right\} = \int_{0}^{E_{m}} D(E_{x}) \zeta dE_{x}$$
$$\zeta = \zeta_{1} - \zeta_{2} \qquad \zeta_{1} = \frac{4\pi m^{2} e}{h^{3}} \int_{0}^{\infty} f(E) dE_{r} \qquad \zeta_{2} = \frac{4\pi m^{2} e}{h^{3}} \int_{0}^{\infty} f(E + eV) dE_{r}$$



Illustration showing current flow between the electrodes.

[Simmons, J. Appl. Phys. 34, 1793, (1963)]

Here we shall refer to Fermi-Dirac distribution function f(E) briefly. Fermi-Dirac distribution function is given by

$$f(E) = \frac{1}{\exp\left[\frac{\mu}{k_B T}\right] + 1} \approx \frac{1}{\exp\left[\frac{(E - E_F)}{k_B T}\right] + 1}$$

where is chemical potential and  $\mu$  becomes  $E_F$  at absolute temperature  $T = 0^{\circ} K(T_{\circ})$ . In terms of physical meaning of f(E), f(E) at  $T = 0^{\circ} K$  is in the range between 0 ~ 1 and is classified into three cases.

$$E < E_F \rightarrow \exp\left[\frac{(E - E_F)}{k_B T}\right] \text{ and then } f(E) = 1$$

$$E = E_F \rightarrow \exp\left[\frac{(E - E_F)}{k_B T}\right] \text{ and then } f(E) = \frac{1}{2}$$

$$E > E_F \rightarrow \exp\left[\frac{(E - E_F)}{k_B T}\right] \text{ and then } f(E) = 0$$

Following complicated mathematical treatment by Simmons, the general equation can be described as follows:



$$J = \frac{4\pi me}{h^3} \left\{ eV \int_0^{\eta - eV} \exp\left[-A\left(\eta + \bar{\phi} - E_x\right)^{1/2}\right] dE_x + \int_{\eta - eV}^{\eta} (\eta - E_x) \exp\left[-A\left(\eta + \bar{\phi} - E_x\right)^{1/2}\right] dE_x \right\}$$

Following complicated mathematical treatment by Simmons, the general equation can be described as follows:

$$U = \frac{e}{2\pi h d^2} \left\{ \overline{\phi} \exp\left(-A\sqrt{\overline{\phi}}\right) - \left(\overline{\phi} + eV\right) \exp\left[-A\sqrt{\overline{\phi} + eV}\right] \right\}$$

The above Eq. is the general formula representing density of tunnel current and the parameters in Eq. are classified by the strength of electric field. For low-voltage range  $(V \approx 0)$  $d = d_0$ ,  $d_0$  is the thin film thickness.

**Another approximation** 

 $J = \left[\frac{3\sqrt{2m\phi_o}}{2d_o}\right] \left(\frac{e}{h}\right)^2 V \exp\left[\frac{4\pi d_o}{h}\sqrt{2m\phi_o}\right] \qquad \qquad J = \left\lfloor\frac{\sqrt{2m\phi_o}}{d_o}\right\rfloor \left(\frac{e}{h}\right)^2 V \exp\left[\frac{4\pi d_o}{h}\sqrt{2m\phi_o}\right]$ 

Well-known equation

For intermediate-voltage range  $(V < \phi_o/e)$ 

 $\boldsymbol{d} = \boldsymbol{d}_{\mathrm{o}} \qquad \qquad \boldsymbol{\overline{\phi}} = \left( \boldsymbol{\phi} - \boldsymbol{e} \boldsymbol{V} / 2 \right)$ 

$$J = \frac{e}{2\pi h d_o^2} \left\{ \left(\phi_o - \frac{eV}{2}\right) \exp\left[-\frac{4\pi d_o}{h} \sqrt{2m\left(\phi_o - \frac{eV}{2}\right)}\right] - \left(\phi_o + \frac{eV}{2}\right) \exp\left[-\frac{4\pi d_o}{h} \sqrt{2m\left(\phi_o + \frac{eV}{2}\right)}\right] \right\}$$

**For high -voltage range**  $(V < \phi_o/e)$ 

$$d = d_o \phi_o / eV \quad \overline{\phi} = \phi_o / 2$$

$$J = \left(\frac{2.2e^3}{8\pi h\phi_o}\right) \left(\frac{V}{d_o}\right)^2 \left\{ \exp\left[-\frac{8\pi d_o}{2.96heV}\sqrt{2m\phi_o^3}\right] - \left(1 + \frac{2eV}{\phi_o}\right) \exp\left[-\frac{8\pi d_o}{2.96heV}\sqrt{2m\phi_o^3}\left(1 + \frac{2eV}{\phi_o}\right)^{1/2}\right] \right\}$$

#### **Exercise**

Let's consider the numerical calculation in low-voltage range. To pursue it, the area of insulation film is defined as *S* and tunneling current and resistance are defined as *I* and *R*. Because of and , *RS* becomes

$$RS = \frac{1}{\left[\frac{\sqrt{2m\phi_o}}{d_o}\right] \left(\frac{e}{h}\right)^2 \exp\left[\frac{4\pi d_o}{h}\sqrt{2m\phi_o}\right]}$$

Assuming Å and  $\phi_o = 1eV$ for exercise of the numerical calculation. *RS* becomes 8.917  $\Omega \bullet \mu m^2$ . The relationship between barrier width ( $d_o$ ) and barrier height ( $\phi_o$ ) is shown below.  $e(electron charge) = 1.602 \ge 10^{-19}(C),$   $m = 9.109 \ge 10^{-31} (kg),$  $h = 6.626 \ge 10^{-4} (J \cdot s)$ 



Let's consider that the dimension of the lower Eq. is current density.

$$J = \left[\frac{\sqrt{2m\phi_o}}{d_o}\right] \left(\frac{e}{h}\right)^2 V \exp\left[\frac{4\pi d_o}{h}\sqrt{2m\phi_o}\right]$$

 $\left[\frac{\sqrt{2m\phi_o}}{d_o}\right] \left(\frac{e}{h}\right)^2 V$  is the dimension of current density as follows:

$$\begin{bmatrix} \frac{C^2 V}{(J \bullet s)^2 m} \sqrt{kgJ} \end{bmatrix} = \begin{bmatrix} \frac{C}{s \bullet m^2} \bullet \frac{CVm}{J^2 s} \sqrt{kg \bullet J} \end{bmatrix} = \begin{bmatrix} \frac{C}{s \bullet m^2} \frac{CV}{J^2} \sqrt{\frac{kg \bullet m}{s^2}} m \bullet J \end{bmatrix}$$
$$= \begin{bmatrix} \frac{C}{s \bullet m^2} \frac{CV}{J^2} \sqrt{N \bullet m \bullet J} \end{bmatrix} = \begin{bmatrix} \frac{C}{s \bullet m^2} \frac{J}{J^2} \sqrt{J^2} \end{bmatrix} = \begin{bmatrix} \frac{C}{s \bullet m^2} \end{bmatrix}$$

 $-\left(\frac{4\pi d_o}{h}\right)\sqrt{2m\phi_o}$  is the dimension of current density as follows:

$$\left[\frac{m}{J \bullet s}\sqrt{kg \bullet J}\right] = \left[\frac{1}{J}\sqrt{\frac{kg \bullet m}{s^2}} m \bullet J\right] = \left[\frac{1}{J}\sqrt{M \bullet m \bullet J}\right] = \left[\frac{1}{J}\sqrt{J^2}\right] = \left[1\right]$$

#### **Thermal fluctuation-induced tunneling effect**

The well-known theory described already is attributed to that the tunneling of electrons is independent of temperature.

As shown already, however, the conductivity of polymer-filler is sensitive to the measured temperature. To solve this problem, one approach was proposed by Sheng in terms of fluctuation-induced tunneling condition.

To do so, Sheng was adopted the average square of thermal fluctuation voltage across the tunnel junction

 $\langle V_T^2 \rangle$  based on the assumption shown in Fig., in which *C* denoting only a small part of the total capacitance  $C_0$  between the two large conducting segments is given as and *R*/2 denotes the resistance connecting the junction capacitor to the rest of the conducting segments.



Schematic tunneling junction is depicted (1, 2180 (1980) as a parallel plate capacitor.

P. Sheng, Phys. Rew B21, 2180 (1980)

When C<<C<sub>o</sub>,  $\langle V_T^2 \rangle$  is given by

$$\left\langle V_{T}^{2} \right\rangle = \int_{0}^{\infty} \frac{4kTR}{(2\pi fCR)^{2} + \left(1 + \frac{C}{C_{o}}\right)^{2}} df = \int_{0}^{\infty} \frac{4kTR}{(2\pi fCR)^{2} + 1} df = 4kTR \sqrt{\frac{1}{(2\pi CR)^{2}} \left[\arctan\left((2\pi fCR)^{2}x\right)\right]_{0}^{\infty}} = \frac{kT}{C} \frac{1}{2}C \left\langle V_{T} \right\rangle^{2} = \frac{1}{2}kT$$

Since the equipartition theory is a direct consequence of the Boltzmann distribution, the above equation suggests that the probability of fluctuations is proportional to  $\exp(-\Delta E/kT)$ , associated with the energy needed to move the system away from equilibrium. For the general case of a capacitor with an externally applied potential  $V_A$ , a deviation of  $\pm V_T$  away from  $V_A$  requires

$$\Delta E = \frac{1}{2}C(V_A \pm V_T) - \frac{1}{2}CV_A^2 \mp CV_T V_A$$

where the first two terms represent the change in the electrostatic energy of the capacitor and the last term gives the work done by the external potential. The net result of  $\Delta E = (1/2)CV_T^2$  means that the normalized function of fluctuation probability for  $0 \le V_T < \infty$  is given by  $a = Ad/8\pi$ 

$$P(V_T) = \sqrt{\frac{2C}{\pi kT}} \exp\left(-\frac{CV_T^2}{2kT}\right) \qquad P(\delta_T) = \sqrt{\frac{4a}{\pi kT}} \exp\left(-\frac{a\delta_T^2}{kT}\right) \qquad \delta_T = V_T/d$$

Following Sheng, the applied field  $\delta_A$  is introduced in addition to  $\delta_T$  and the two total fields must be considered. At any given value of  $|\delta_T|$ ,

$\delta_T + \delta_A$	in the same direction			
$\delta_T - \delta_A$	in the opposite direction			

When  $\delta_T + \delta_A$  and the equal possibility of the occurrence, the net tunneling current along the direction of the applied field is given by

$$\Delta j = \frac{1}{2} \left[ j \left( \delta_T + \delta_A \right) - j \left( \delta_T - \delta_A \right) \right]$$

The partial conductivity  $\sum (\delta_T)$  can be defined as

$$\begin{split} \sum \left( \delta_T \right) &= \lim_{\delta_A \to 0} \frac{\Delta j}{\delta_A} \\ &= \lim_{\delta_A \to 0} \frac{\frac{d}{d\delta_A} \left( \frac{1}{2} \left[ j \left( \delta_T + \delta_A \right) - j \left( \delta_T - \delta_A \right) \right] \right)_{\delta_A = 0}}{\left( \delta_A \right)'} = \frac{\left( \frac{1}{2} \left[ j \left( \delta_T + \delta_A \right) - j \left( \delta_T - \delta_A \right) \right] \right)_{\delta_A = 0}}{1} \\ &= j' \left( \delta_T \right) = \frac{d j \left( \delta_T \right)}{d\delta_T} \end{split}$$

The fluctuation-induced tunneling conductivity  $\sigma$  of the junction is then obtained by thermal averaging  $\sum (\delta_T)$  as follows:

$$\sigma = \int_0^\infty P(\delta_T) \sum (\delta_T) d\delta_T$$
$$= \int_0^\infty P(\delta_T) \frac{dj(\delta_T)}{d\delta_T} d\delta_T$$

Through very complicated mathematical treatment, the current density can be obtained as follows:

$$j(\varepsilon) = \frac{\pi m e}{h^3} \int_{-\infty}^{\infty} D(E,\varepsilon) \Biggl[ kT \ell n \Biggl( \frac{1 + \exp(-E/kT)}{1 + \exp[-(E + e\varepsilon\delta_o d/kT)]} \Biggr) \Biggr] dE$$
  

$$\Theta(E) = kT \ell n \Biggl( \frac{1 + \exp(-E/kT)}{1 + \exp[-(E + e\varepsilon\delta_o d)/kT]} \Biggr) \begin{cases} 0 & E > 0 \\ E & -e\varepsilon\delta_o d < E < 0 \\ -e\varepsilon\delta_o d & E < -e\varepsilon\delta_o d \end{cases}$$
  

$$D(E,\varepsilon) = \Biggl\{ \exp[-F(E,\varepsilon)], \quad E \le U_m \quad or \quad (\delta < \delta_o) \\ 1, \quad E > U_m \quad or \quad (\delta > \delta_o) \end{cases}$$
  

$$F(E,\varepsilon) = \frac{2\pi d\sqrt{2mU_o}}{h} \int_{s_1}^{s_2} \sqrt{\frac{U(u,\varepsilon) - E}{U_o}} du$$

Based on the concept by Simmons, the accurate potential barrier function is expressed by Sheng as follows:

$$U(u,\overline{\delta}) = U_o \left[ 1 - \frac{\lambda}{u(1-u)} - \overline{\delta}u \right]$$
(1)

where u = x/d is the reduced spatial variation and x is the distance from the left surface of the junction.  $U_o$ is height of the rectangular potential barrier in the absence of image-force correction and

$$\delta_U = U_o / ed$$
  $\lambda = \frac{0.795e^2}{4dKU_o}$ 



 $\lambda$  is the dimensionless parameter governing the amount of image-force correction and the barrier shape, in which *e* is the electric charge and *K* is the dielectric constant of the insulating barrier. The potential representing as Eq. defined to be zero corresponds to Fermi level of the conducting region. The *u*\* value providing the maximum  $U_m = U(u^*, \overline{\delta})$  of Eq. (1) is defined by  $(\partial U / \partial u)_{\max^*} = 0$  At  $U_m = 0$ ,  $\overline{\delta} = \overline{\delta}_{\sigma}$ . A new dimensionless parameter is defined as  $\varepsilon = \overline{\delta} / \overline{\delta}_{o}$ .

 $\overline{\delta} = \overline{\delta}_{a}$ 

 $(\varepsilon < 1)$ 

$$j(\varepsilon) = \frac{\pi m e}{h^3} \int_{-\infty}^0 D(E,\varepsilon) \Theta(E) dE = \frac{\pi m e}{h^3} \left( \frac{U_o}{2\chi d\eta_o(\varepsilon)} \right)^2 \exp\left[-2\chi d\xi(\varepsilon)\right]$$

 $(\varepsilon > 1)$ 

$$j(\varepsilon) = \frac{\pi m e}{h^3} \left[ \frac{U_m^2}{2} + \left( \frac{U_o}{2\chi d\eta_o(\varepsilon)} \right)^2 \left( 1 - \frac{2\chi d}{U_o} \eta_1(\varepsilon) V_m \right) \right]$$
$$= \frac{\pi m e U_o^2}{4\chi^2 d^2 h^3} \left[ 9.68\lambda^2 \chi^2 d^2 \overline{\delta_o^2} (1 - \varepsilon)^2 + \frac{1}{\eta_1^2(\varepsilon)} - \frac{4.4\chi d\lambda \overline{\delta_o} (1 - \varepsilon)}{\eta_1(\varepsilon)} \right]$$

$$\sum(\varepsilon) = \frac{1}{\delta_o} \frac{dj(\varepsilon)}{d\varepsilon} = \begin{cases} \sum_{o} (\varepsilon) \exp\left[-2\delta d\xi(\varepsilon)\right] & \varepsilon \le 1\\ \sum_{1} (\varepsilon) & \varepsilon > 1 \end{cases}$$

$$\begin{split} j(\varepsilon) &= j_o \exp\left[-2\chi d\xi(\varepsilon)\right] = \frac{j_{oo}}{\eta_o^2(\varepsilon)} \exp\left[-2\chi d\xi(\varepsilon)\right] & \delta < \delta_o \quad (\varepsilon < 1) \\ \sum(\varepsilon) &= \frac{1}{\delta_o} \frac{dj(\varepsilon)}{d\varepsilon} = \frac{1}{\delta_o} \frac{dj_o(\varepsilon) \exp\left[-2\chi d\xi(\varepsilon)\right]}{d\varepsilon} & j_o = \frac{\pi me}{h^3} \left(\frac{U_o}{2\chi d\eta_o(\varepsilon)}\right)^2 = \frac{j_{oo}}{\eta_o(\varepsilon)^2} \\ &= \frac{1}{\delta_o} \left\{ \exp\left[-2\chi d\xi(\varepsilon)\right] \frac{dj_o}{d\varepsilon} + j_o(\varepsilon) \exp\left[-2\chi d\xi(\varepsilon)\right] \frac{d\left[-2\chi d\xi(\varepsilon)\right]}{d\varepsilon} \right\} \\ &= \frac{\exp\left[-2\chi d\xi(\varepsilon)\right]}{\delta_o} \left\{ \frac{d\left(\frac{j_{oo}}{\eta_o^2(\varepsilon)}\right)}{d\varepsilon} + j_o(\varepsilon) \frac{d\left[-2\chi d\xi(\varepsilon)\right]}{d\varepsilon} \right\} \\ &= -\frac{\exp\left[-2\chi d\xi(\varepsilon)\right]}{\delta_o} \left\{ \frac{2j_{oo}}{\eta_o^2(\varepsilon)} \frac{d\left[\eta_o(\varepsilon)\right]}{d\varepsilon} + j_o(\varepsilon)2\chi d\frac{d\xi(\varepsilon)}{d\varepsilon} \right\} \\ &= -\frac{\exp\left[-2\chi d\xi(\varepsilon)\right]}{\delta_o} \left\{ \frac{2j_{oo}}{\eta_o^2(\varepsilon)} \frac{d\left[\eta_o(\varepsilon)\right]}{d\varepsilon} + \frac{j_{oo}}{\eta_o^2(\varepsilon)} 2\chi d\frac{d\xi(\varepsilon)}{d\varepsilon} \right\} \\ &= -\frac{\exp\left[-2\chi d\xi(\varepsilon)\right]}{\delta_o} \left\{ \frac{2j_{oo}}{\eta_o^2(\varepsilon)} \frac{d\left[\eta_o(\varepsilon)\right]}{d\varepsilon} + \chi d\frac{d\xi(\varepsilon)}{d\varepsilon} \right\} \exp\left[-2\chi d\xi(\varepsilon)\right] \\ &= -2\frac{j_{oo}}{\delta_o} \frac{1}{\eta_o^2(\varepsilon)} \left\{ \frac{1}{\eta_o(\varepsilon)} \frac{d\left[\eta_o(\varepsilon)\right]}{d\varepsilon} + \chi d\frac{d\xi(\varepsilon)}{d\varepsilon} \right\} \exp\left[-2\chi d\xi(\varepsilon)\right] \\ &= -\frac{\pi me U_o^2}{2h^3 \chi d^2 [\eta_o(\varepsilon)]^2} \left\{ \frac{1}{\eta_o(\varepsilon)} \frac{d\left[\eta_o(\varepsilon)\right]}{d\varepsilon} + \chi d\frac{d\xi(\varepsilon)}{d\varepsilon} \right\} \exp\left[-2\chi d\xi(\varepsilon)\right] \\ &= \sum_o (\varepsilon) \exp\left[-2\chi d\xi(\varepsilon)\right] \end{aligned}$$

As pointed by Sheng, the calculation of the junction conductivity must involve thermal averaging  $\sum(\varepsilon)$  as expressed already. (Important)

$$\begin{split} \sigma &= \delta_o \int_0^\infty P(\varepsilon_T) \sum (\varepsilon_T) d\varepsilon_T \\ &= \delta_o \int_0^1 P(\varepsilon_T) \sum (\varepsilon_T) d\varepsilon_T + \delta_o \int_1^\infty P(\varepsilon_T) \sum (\varepsilon_T) d\varepsilon_T \\ &= \delta_o \int_0^1 \left(\frac{4a}{\pi kT}\right)^{\frac{1}{2}} \exp\left(-\frac{a\varepsilon_T^2 \delta_o^2}{kT}\right) \sum_o (\varepsilon_T) \exp\left[-2\chi d\xi(\varepsilon_T)\right] d\varepsilon_T \\ &+ \delta_o \int_1^\infty \left(\frac{4a}{\pi kT}\right)^{\frac{1}{2}} \exp\left(-\frac{a\varepsilon_T^2 \delta_o^2}{kT}\right) \sum_1 (\varepsilon_T) d\varepsilon_T \\ &= \left(\frac{4a\delta_o}{\pi kT}\right)^{\frac{1}{2}} \left[\int_0^1 \sum_o (\varepsilon_T) \exp\left(-\frac{a\delta_o^2}{kT} \varepsilon_T^2 - 2\chi d\xi(\varepsilon_T)\right) d\varepsilon_T + \int_1^\infty \exp\left(-\frac{a\delta_o^2}{kT} \varepsilon_T^2\right) \sum_1 (\varepsilon_T) d\varepsilon_T \right] \\ &= \left(\frac{4a\delta_o^2}{\pi kT}\right)^{\frac{1}{2}} \left[\int_0^1 \sum_o (\varepsilon_T) \exp\left(-\frac{a\delta_o^2}{kT} \varepsilon_T^2 - 2\chi d\xi(\varepsilon_T)\right) d\varepsilon_T + \int_1^\infty \exp\left(-\frac{a\delta_o^2}{kT} \varepsilon_T^2\right) \sum_1 (\varepsilon_T) d\varepsilon_T \right] \\ &= \left(\frac{4T_1}{\pi T}\right)^{\frac{1}{2}} \left[\int_0^1 \sum_o (\varepsilon_T) \exp\left(-\frac{T_1}{T} \varepsilon_T^2 - \frac{T_1}{T_o} \varphi(\varepsilon_T)\right) d\varepsilon_T + \int_1^\infty \sum_1 (\varepsilon_T) \exp\left(-\frac{T_1}{T} \varepsilon_T^2\right) d\varepsilon_T \right] \\ &\quad T_1 = \frac{a\delta_o^2}{k} \qquad T_o = \frac{T_1}{2\chi d\xi(0)} \qquad \varphi(\varepsilon) = \frac{\xi(\varepsilon)}{\xi(0)} \qquad \varphi(0) = 1 \qquad \varphi(1) = 0 \end{split}$$

$$\sigma = \sigma_o \exp\left[-\frac{T_1}{T} (\varepsilon^*)^2 - \frac{T_1}{T_o} \varphi(\varepsilon^*)\right]$$

where

$$\sigma_{o} = \exp\left[\frac{T_{1}}{T}(\varepsilon^{*})^{2} + \frac{T_{1}}{T_{o}}\varphi(\varepsilon^{*})\right]$$

$$\times \left(\frac{4T_{1}}{\pi T}\right)^{\frac{1}{2}} \left[\int_{0}^{1} \sum_{o} (\varepsilon_{T}) \exp\left(-\frac{T_{1}}{T}\varepsilon_{T}^{2} - \frac{T_{1}}{T_{o}}\varphi(\varepsilon_{T})\right) d\varepsilon_{T} + \int_{1}^{\infty} \sum_{1} (\varepsilon_{T}) \exp\left(-\frac{T_{1}}{T}\varepsilon_{T}^{2}\right) d\varepsilon_{T}\right]$$

 $\sigma_o$  is treated as a constant.

Furthermore, Sheng proposed a simple equation which has been adopted in a number of papers. A parabolic potential barrier is defined as follows:

$$U_{p} = U_{o} [u(1-u) - \varepsilon \overline{\delta}_{o} u]$$

$$\varphi(\varepsilon) = \frac{\xi(\varepsilon)}{\xi(0)} = \frac{\int_{0}^{1-\varepsilon} [u(1-u) - \varepsilon u]^{\frac{1}{2}} du}{\int_{0}^{1} [u(1-u)]^{\frac{1}{2}} du} = (1-\varepsilon)^{2} \qquad f(\varepsilon) = -\frac{T_{1}}{T} \varepsilon^{2} - \frac{T_{1}}{T_{o}} \varphi(\varepsilon) = -\frac{T_{1}}{T} \varepsilon^{2} - \frac{T_{1}}{T_{o}} (1-\varepsilon)^{2}$$

$$\frac{df(\varepsilon)}{d\varepsilon} |\varepsilon^{*} = 0 \qquad \varepsilon^{*} = \frac{T}{T+T_{o}} \qquad \sigma(T) \propto \exp\left[-\frac{T_{1}}{T+T_{o}}\right]$$

$$\varepsilon_T = \varepsilon^*$$

$$\sigma = \left(\frac{4T_1}{\pi T}\right)^{\frac{1}{2}} \left[\int_0^1 \sum_{o} \left(\varepsilon_T\right) \exp\left(-\frac{T_1}{T}\varepsilon_T^2 - \frac{T_1}{T_o}\varphi(\varepsilon_T)\right) d\varepsilon_T + \int_1^\infty \sum_{i} \left(\varepsilon_T\right) \exp\left(-\frac{T_1}{T}\varepsilon_T^2\right) d\varepsilon_T\right]$$

By Sheng, the functions  $-\varphi(\varepsilon_T) \rightarrow -10\varphi(\varepsilon_T)$  $-\varepsilon_T^2 \rightarrow -10\varepsilon_T$ 

$$\sigma = \sigma_o \exp\left[-\frac{T_1}{T}(\varepsilon^*)^2 - \frac{T_1}{T_o}\varphi(\varepsilon^*)\right]$$

As the summation of the two factors shown as a dashed line takes a maximum at  $\mathcal{E}_T = \mathcal{E}^*$ , the first integrated values in Eq. also takes a maximum. The numerical calculation indicated that the first term is much larger



indicated that the first term is much larger than the second term.

$$\sigma_{o} = \exp\left[\frac{T_{1}}{T}(\varepsilon^{*})^{2} + \frac{T_{1}}{T_{o}}\varphi(\varepsilon^{*})\right]$$

$$\times \left(\frac{4T_{1}}{\pi T}\right)^{\frac{1}{2}} \left[\int_{0}^{1} \sum_{o} (\varepsilon_{T}) \exp\left(-\frac{T_{1}}{T}\varepsilon_{T}^{2} - \frac{T_{1}}{T_{o}}\varphi(\varepsilon_{T})\right) d\varepsilon_{T} + \int_{1}^{\infty} \sum_{1} (\varepsilon_{T}) \exp\left(-\frac{T_{1}}{T}\varepsilon_{T}^{2}\right) d\varepsilon_{T}\right]$$

$$\sigma = \sigma_o \exp\left[-\frac{T_1}{T}(\varepsilon^*)^2 - \frac{T_1}{T_o}\varphi(\varepsilon^*)\right]$$
$$U(u,\overline{\delta}) = U_o\left[1 - \frac{\lambda}{u(1-u)} - \overline{\delta}u\right]$$

To pursue simple analysis, Sheng proposed the parabolic potential barrier Up in stead of the above Eq.  $\sim S^2$ T

$$U_{p} = U_{o}[u(1-u) - \varepsilon \overline{\delta}_{o}u] \qquad T_{1} = \frac{d\sigma_{o}}{k} \qquad T_{o} = \frac{T_{1}}{2\chi d\xi(0)}$$
$$\varphi(\varepsilon) = \frac{\xi(\varepsilon)}{\xi(0)} = \frac{\int_{0}^{1-\varepsilon} [u(1-u) - \varepsilon u]^{\frac{1}{2}} du}{\int_{0}^{1} [u(1-u)]^{\frac{1}{2}} du} = (1-\varepsilon)^{2} \qquad \varphi(\varepsilon) = \frac{\xi(\varepsilon)}{\xi(0)}$$
$$f(\varepsilon) = -\frac{T_{1}}{T} \varepsilon^{2} - \frac{T_{1}}{T_{o}} \varphi(\varepsilon) = -\frac{T_{1}}{T} \varepsilon^{2} - \frac{T_{1}}{T_{o}} (1-\varepsilon)^{2} \qquad \frac{df(\varepsilon)}{d\varepsilon} |\varepsilon^{*} = 0 \qquad \varepsilon^{*} = \frac{T}{T+T_{o}}$$

 $\sigma(T) \propto \exp\left[-\frac{T_1}{T+T_o}\right]$  The popular equation to evaluate temperature dependence of polymer-filler composites by tunneling current<sub>o</sub>

#### **Big Problem about** d

## **Current vs. voltage by DC measurement**



The surfaces were buffed by sandpaper. VGCF VGCE  $(d)^{\mathsf{D}}$ 3.11 vol% D(d) = 1.20 nm6.28 vol% D(d) = 1.00 nmD or d

A : area

With increasing

- 1) vol% content
- 2) Temperature
- 3) Voltage



 $\sigma = \left(\frac{4T_1}{\pi T}\right)^{\frac{1}{2}} \left[ \int_0^1 \sum_{\sigma} (\varepsilon_T) \exp\left(-\frac{T_1}{T} \varepsilon_T^2 - \frac{T_1}{T_o} \varphi(\varepsilon_T)\right) d\varepsilon_T + \int_1^\infty \sum_{\tau} (\varepsilon_T) \exp\left(-\frac{T_1}{T} \varepsilon_T^2\right) d\varepsilon_T \right]$ 

D (d) = 1.200 nm 3.11 vol% D (d) = 1.000 nm 6.28 vol%

$$(T) \propto \exp\left[-\frac{T_1}{T+T_o}\right]$$
 **Not good**

D(d) = 0.000502nm	3.11 vol%
D (d) = 0.000329 nm	6.28 vol%

Out of the common sense of polymer science.

PE is heat resistant polymer and the thermal expansion of bulk is almost zero. Then, the distance between adjacent VGCFs is constant independent of temperature. The increase in conductivity (current) with temperature is due to an increase in surface area (A) over which most of tunneling effect occurs.

#### How to evaluate electron tunneling in relation to sample morphology?

- 1) the interference resistance between electrode and composite,
- 2) resistance of the grain boundary region between filler and polymer
- 3) filler resistance.

To classify them, the curve fittings between experimental complex impedance and that calculated by three-unit model and three kinds of resistivity was determined at frequency = 0 (DC component) and the distance between adjacent fillers was determined.





## The corresponding parameters from the simulating results for the composite with 6.28 vol% VGCF

<i>T</i> (°C)	25	40	80	120	160
$R_1(\Omega)$	30	30	30	30	30
$C_1 ({ m F}  imes 10^{-3})$	89.5	89.9	90.0	95.0	100
$R_2 \left( \Omega  imes 10^4  ight)$	1.62	1.55	1.42	1.36	0.94
C <sub>2</sub> (pF)	783	800	793	890	920
α	0893	0.888	0.883	0.874	0.865
$R_{3}(\Omega)$	310	308	306	304	300
$C_2 (\mathrm{pF}  imes 10^4)$	3.40	3.51	3.80	4.08	4.18
β	0.6548	0.6500	0.6248	0.6304	0.6504





Interference resistance between electrode and composites

VGCF/PI boundary resistance

VGCF resistance





 $\kappa_{\rm DC}$ , corresponding to the DC component (frequency  $\rightarrow 0$  Hz) of AC conductivity, is represented as  $\varepsilon_0/\{C_0(R_1 + R_2)\}$  for the 3.11 vol % VGCF content  ${\rm and}\varepsilon_0/\{C_0(R_1 + R_2 + R_3)\}$  for the 6.28 vol % VGCF content.  $R_2 >> R_1$  two units

 $R_2 >> R_1, R_3$  three units

 $\kappa_{\rm DC}$ , listed in previous Table are hardly affected by the first and third units and are governed by the second unit associated with a contact region between adjacent VGCFs. Furthermore, the value of  $\kappa_{\rm DC}$  increases with increasing temperature.

The *D* and *A* values evaluated by AC current are equal to those by DC current. The D values depend on the VGCF content but are independent of temperature. The increase in  $\kappa_{DC}$  is in connection with the value of A associated with electron transfer area.

Furthermore, the values are independent of the electric field direction.

3.11 vol%D = 1.20 nm6.28 vol%D = 1.00 nm

A : area With increasing

- 1) vol% content,
- 2) Temperature
- 3) Voltage



The surfaces were buffed by sandpaper.



# Temperature dependence of parameters D, A and at 0.1 and 0.5V calculated by using $\kappa_{DC}$ .



	<i>T</i> (°C)	λ	D (nm)	A (nm <sup>2</sup> )	λ	<b>D</b> (nm)	A (nm <sup>2</sup> )
		0.1V	0.1V	0.1V	0.5V	0.5V	0.5V
	25	0.02200	1.20	1.621	0.02216	1.20	1.740
	40	0.02200	1.20	1.701	0.02216	1.20	1.752
3.11 vol%	80	0.02200	1.20	1.931	0.02216	1.20	1.912
	120	0.02200	1.20	1.941	0.02216	1.20	2.000
	160	0.02200	1.20	1.977	0.02216	1.20	2.135
	<i>T</i> (°C)	λ	<i>D</i> (nm)	A (nm <sup>2</sup> )	λ	<b>D</b> (nm)	A (nm <sup>2</sup> )
		0.1V	0.1V	0.1V	0.5V	0.5V	0.5V
	25	0.02468	1.00	2.010	0.02515	1.00	2.360
	40	0.02489	1.00	2.330	0.02531	1.00	2.510
6.28 vol%	80	0.02498	1.00	2.430	0.02546	1.00	2.780
	120	0.02501	1.00	2.500	0.02568	1.00	2.860
	160	0.02598	1.00	2.750	0.02582	1.00	2.980

Most of natural science students have learned "Materials Science" as one of their undergraduate course subjects. Certainly, they have acquired knowledge about physical and chemical properties of materials and have been learned the concept of Schrödinger equation in their courses concerning the probability density of electrons in a hydrogen-like atom and the eigenvalue of energy. However, most of the polymer scientists who have majored polymer physics in their graduate course show little interest for Schrödinger equation to investigate electric properties of conductive polymers and conductive filler-polymer composites. The analyses of polymer scientists have been carried out qualitatively by using the simplified final equations proposed by solid physicists and electrical engineers. They have analyzed their results based on the conductivity of the filler-polymer composites by using the theoretical tunneling analyses established for conductive (or semi-conductive)-insulator-conductive (or semi-conductive) system.

The present talk introduced slight detailed treatments about electric and dielectric properties for filler-polymer composites in terms of elementary quantum mechanics.

