Apparent metal-insulator transition in disordered carbon fibers

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In a previous report [Phys. Lett. A **216**, 178 (1996)] we phenomenologically considered the conduction mechanism of a highly disordered carbon system. In this article a metal-insulator transition is investigated based on our theory for the disordered system. Our results for the temperature-dependent conductivity show an apparent metal-insulator transition and are in good agreement with experimental results in disordered carbons.

In a previous report[1] we proposed a mechanism, hopping conductivity, for disordered systems using the result of quantum chaos.[2–4] In this paper we extend it to show the metal-insulator transition and reproduce the experimental results of Kuriyama[5] by adding another assumption.

Kuriyama and Dresselhaus[6–9] have performed experiments on the electrical and structural properties of activated carbon fibers (ACF's). As it is known[10] that ACF's are highly disordered carbon systems (HDCS's), these experimental results have shed new light on disordered system. In Refs. 5 and 7, Kuriyama and Dresselhaus found that there is a metal-insulator transition depending upon the randomness of the system.

Even in the field of the disordered system, one sometimes phenomenologically introduces a band diagram for the noncrystal system.[11] However, the band spectrum should be defined only for the electron in a crystal and the use of ''band spectrum in noncrystal systems'' is somewhat nonsensical, even though such a standpoint has been given many physical interpretations and proper predictions. Kuriyama proposed an ingenious phenomenological model to explain the temperature dependence of the conductivity (TDC) in ACF's.[5]

The present authors have also attempted to elucidate the conduction mechanism in the disordered system, along the lines of quantum mechanics. In the previous report,[1] we proposed a mechanism for the hopping conductivity of the disordered system from more microscopic aspects. Our theoretical estimate (based on the model) of the TDC for the ACF's partially agrees well with Kuriyama's experimental results.[5] However, since our TDC formula exhibits the property that the conductivity vanishes at zero temperature, we made no mention of the metal-insulator transition in Ref. 1. In this paper, we attempt to investigate the metal-insulator transition seen in ACF's,[5,7,9] based upon our proposed conduction mechanism. By modifying our TDC formula proposed in Ref. 1, we can show that our new formula [Eq. (17)] exhibits an apparent metal-insulator transition and reproduces the experimental results.

As it is well known that the ACF's consist of small graphite granules, we can regard each electric state in each granule as being independent, and that electrons in granules can hop to adjacent granules, so that electric current can flow in the system. Since the quantum mechanical properties of electrons in a small granule obey the law of quantum chaos, these energy levels must be expressed in terms of the random matrix.[2–4] Since each electric property obeys the energy splitting law, the global properties may also be influenced by the local properties of each granules. Accordingly, we introduced an assumption, and we demonstrated that the TDC can be expressed in terms of the integral of the Wigner distribution. Our theoretical estimate,[1] based on this TDC formula, closely agrees with the experimental results.[5]

In order to elucidate a metal-insulator transition observed in ACF's, we will employ the same model as proposed in Ref. 1.

(i) The ACF is arranged between two electrodes.

(ii) In HDCS's, graphite granules (clusters in ACF's), whose size is controlled by annealing and is characterized by their average radius R (of the order of nm), are disposed at random in the ACF.

(iii) The local properties of each granule (as a theoretical model) resemble to those of pure graphite, that is, a semimetal.

(iv) The wave function of an electron in each granule is nearly localized with each granule as a quantum box.

(v) Electrons in each quantum box (or granule) are transported by thermal hopping.

(vi) The coherent length of each granule is characterized by ξ.

Let us briefly review the conduction mechanism proposed in Ref. 1 based on the above model. An electron hops between adjoining granules. The Fermi energy of the ith granule roughly agrees with that of the adjacent one (the jth granule). Near zero temperature, the electron at the Fermi level of the ith granule hops to the above vacant level of the Fermi level in the jth granule, so that electric current flows between them. Let us denote the energy gap by E_{G}:

$$E_{\mathrm{G}}^{i,j} := |E_{\mathrm{C}}^{j} - E_{\mathrm{F}}^{i}|, \tag{1}$$

where E_{C}^{j} is the energy level just above the Fermi energy E_{F}^{j} of the jth granule.

The local TDC of the electric connection between the granules i and j is then given by

$$\sigma_{i,j} \propto \exp(-E_{\mathrm{G}}^{i,j}/k_{\mathrm{B}}T), \tag{2}$$

where k_{B} is the Boltzmann constant and T is the absolute temperature. Such adjacent granules compose electric net-

works between the electrodes. The nature of the electric current is that it flows along the *easiest* paths of all possible electric paths among the links between the electrodes. In all percolation paths $\{C_a\}$ from one electrode to another, there exists a set of the most realizable paths $\Gamma_0 := \{C_a^0\}$.

The conductivity σ_a along a path C_a^0 of Γ_0 can be thus determined by the sum of the resistance in each connection of a pair of granules, $1/\sigma_{i,i+1}$:

$$\sigma_a = \left(\sum_i \frac{1}{\sigma_{i,i+1}} \right)^{-1}. \tag{3}$$

If the deviation of each conductivity $\sigma_{i,i+1}$ is large, we may approximate it as

$$\sigma_a \approx \left(\max_i \frac{1}{\sigma_{i,i+1}} \right)^{-1}. \tag{4}$$

In general, the energy levels in ith and jth granules are *not* correlated. Therefore the difference of energy levels (denoted by m level at the ith and n level at the jth granules), $E_{m,n}^{i,j} := |E_m^i - E_n^j|$, obeys the Poisson distribution[1]

$$D_{\text{level}}^{\text{Poisson}}(\delta E)d(\delta E) = \exp(-\delta E/a)d(\delta E), \tag{5}$$

where a is an appropriate parameter. Most parts of the energy gap E_G's obey this distribution. If E_G vanishes, most contributions to the local conductivity are finite even near zero temperature [see Eq. (2)]. However, the *difference of the Fermi levels* of the ith and jth granules $|E_F^i - E_F^j|$ also obeys the Poisson distribution (5). We could also find pairs whose Fermi levels agree with each other from the probability consideration. In such a case, we can approximate $E_G^{i,j} := |E_C^j - E_F^i| \approx |E_C^j - E_F^j| =: E_G^{j,j}$, so that we have

$$\max_i \frac{1}{\sigma_{i,i+1}} \approx \max_i \exp(-E_G^{i,i}/k_B T). \tag{6}$$

As the conductivity of each parallel path Γ_0 is independent, the summation over them simply gives the total conductivity. Accordingly the total conductivity of the HDCS is then given in terms of the distribution $D_{\text{level}}(E_G)dE_G$ of $E_G^{i,i}$ as

$$\sigma(T) = \sigma_0^{(0)} \int dE_G D_{\text{level}}(E_G)\exp(-E_G/k_B T). \tag{7}$$

Here $\sigma_0^{(0)}$ represents the number of conductive paths. Even though we regarded it as a constant in Ref. 1, we will later assume that it has a weak ''temperature'' dependence.

Next we consider the effect of the coherent length ξ as illustrated in Fig. 1. The coherent length is defined at zero temperature. As we will show later, ξ is *not* so important in our model, but in order to assert that ξ is not important, let us investigate it here. We consider the effect of the coherent length ξ in a three-dimensional (bulk) carbon system, which is not completely graphite but has defects. A defect makes an electron localize in its vicinity. The wave function around it is asymptotically expressed in terms of ξ and a certain length $\delta(\delta < \xi)$ as[12]

$$\psi \sim A \exp(-|\boldsymbol{x} - \boldsymbol{x}_0|/\xi) \quad \text{for} \quad |\boldsymbol{x} - \boldsymbol{x}_0| > \delta. \tag{8}$$

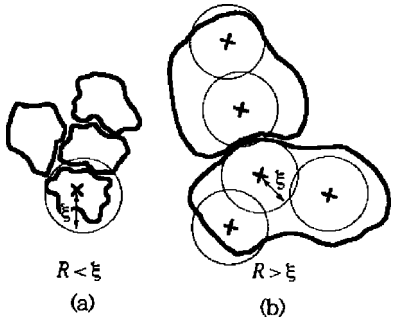

FIG. 1. Average radius of granules R and that of coherent lengths ξ as characteristic lengths in the system: (a) is the case for $\xi > R$ and (b) is that for $\xi < R$. In the (a) case, the electron feels the boundary of granule and the energy levels obey the Wigner distribution. In the (b) case, the electron is localized around a defect, and in the conduction, it also hops among these localized states of granules.

Here, $\boldsymbol{x}$ and $\boldsymbol{x}_0$ indicate, respectively, the position of electron and defect in a granule.

On the other hand, there is another typical length in our system, that is, the size of those granules from the viewpoint of a quantum mechanical study. We denote the average radius of the granules by R, which need not be identified completely with that estimated from structural studies. Then we have two cases (a) $R < \xi$ and (b) $R > \xi$ as seen in Fig. 1.

When the average radius R of granules is smaller than a coherent length ξ (i.e., $R < \xi$), the electron in a granule feels the boundary of the granule. In the classical picture, its motion in a box (granule) with irregular-shape boundary is chaotic. Thus, in the quantum mechanical picture, its energy level should obey the random matrix theory. In other words, for the $\xi > R$ case, $D_{\text{level}}(E_G)$ can be expressed in terms of the Wigner distribution $D_{\text{level}}^{\text{Wigner}}(E_G)$:[2–4]

$$D_{\text{level}}^{\text{Wigner}}(E_G)dE_G = 2(E_G/\alpha^2)\exp(-E_G^2/\alpha^2)dE_G. \tag{9}$$

In such a case, from Eq. (7) the total conductivity $\sigma^{\text{Wigner}}(T)$ is given by

$$\begin{aligned}\sigma^{\text{Wigner}}(T) &= \sigma_0^{(0)} \int dE_G D_{\text{level}}^{\text{Wigner}}(E_G)\exp(-E_G/k_B T) \\ &= \sigma_0^{(0)} \left[1 - \sqrt{\pi}\, \frac{\alpha}{2k_B T} \exp\left(\frac{\alpha}{2k_B T} \right)^2 \operatorname{erfc}\left(\frac{\alpha}{2k_B T} \right) \right].\end{aligned} \tag{10}$$

Here α is given by

$$\alpha \sim E_F/N_i \sim \frac{E_F}{n_0(4\pi R^3/3)}, \tag{11}$$

where E_F is the Fermi energy and n_0 is the number of electrons per unit volume. For typical values,[9] $R = 3$ nm, $E_F = 0.0053$ eV, and $n_0 = 3 \times 10^{24}$ m^{-3}, we have

$$\alpha = 181 \text{ K} = 15.6 \text{ meV}. \tag{12}$$

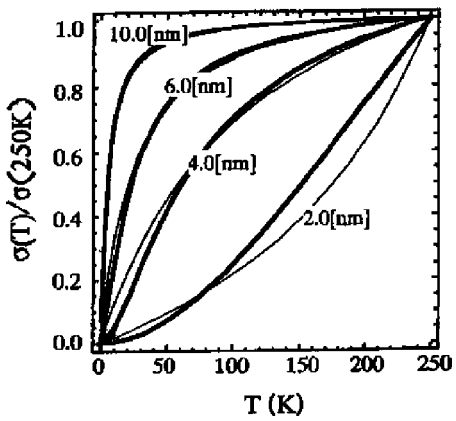

FIG. 2. The temperature dependence of normalized conductivity for σ^{Wigner} and σ^{Poisson}. Thin lines correspond to the curves for σ^{Poisson} and thick ones are those for σ^{Wigner}. They are parametrized by ξ or R, respectively. ξ and R are taken for 2 nm, 4 nm, 6 nm, and 10 nm.

We have assumed that the granule is a filled ball for the sake of simplicity. This result is in good agreement with the experimental results of Kuriyama[5] as we showed in Ref. 1.

Next we consider the case for $R>\xi$. In this case, the electron *cannot* feel the whole boundary of the granule; neither can it know the global shape of the granule. Hence its kinematic behavior is *not* chaotic. Accordingly the energy interval of the granule is expressed in terms of the Poisson distribution[2–4]

$$D_{\text{level}}^{\text{Poisson}}(E_{\text{G}})dE_{\text{G}}=\frac{1}{\gamma(\xi)}\exp[-E_{\text{G}}/\gamma(\xi)]dE_{\text{G}}, \quad (13)$$

and does not obey the Wigner distribution at all in this case. Here, γ is given by

$$\gamma(\xi)\sim E_{\text{F}}/N_i\sim\frac{E_{\text{F}}}{n_0(4\pi\xi^3/3)}. \quad (14)$$

Using Eq. (13) along with Eq. (14), the total conductivity (7) is then given by

$$\sigma^{\text{Poisson}}(T)=\sigma_0^{(0)}\int dE_{\text{G}}D_{\text{level}}^{\text{Poisson}}(E_{\text{G}})\exp(-E_{\text{G}}/k_{\text{B}}T)$$

$$=\sigma_0^{(0)}\frac{k_{\text{B}}T}{k_{\text{B}}T+\gamma(\xi)}. \quad (15)$$

The plots for $\sigma^{\text{Wigner}}(T)$ and $\sigma^{\text{Poisson}}(T)$ are shown in Fig. 2, which are parametrized by R and ξ, respectively. Both behave in a similar manner. Especially, when R and ξ are greater than 10 nm, both cases coincide with each other even quantitatively. However, for a small R and ξ, their shape is different. As we showed in Ref. 1, the experimental results agree well with the case for the use of the Wigner distribution, i.e., σ^{Wigner} for a small radius $R(<10$ nm). Thus for a small radius case, we assert that the conduction mechanism there is based upon the chaotic process.

On the other hand, for $R,\xi>10$ nm, we cannot distinguish between them; nor can we decide their conduction mechanism. We cannot discriminate between the conduction mechanisms. It should, however, be emphasized that there

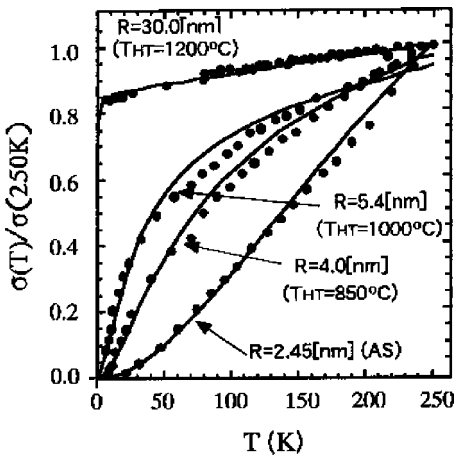

FIG. 3. The temperature dependence of normalized conductivity. The dotted points show the experimental results of the temperature dependence on normalized conductivity $\sigma(T)/\sigma(250\ \text{K})$ for as-prepared (AS) and heat-treated ACF's (Fig. 1 in Ref. 5). Fits of these points are given by curves, whose fitting parameters R and ϵ in Eq. (17) are $R=2.45$ nm, 4.00 nm, 5.40 nm, 30.0 nm, and $\epsilon^{-1}=1.5\times10^3\ \text{K}^{-1}$.

appears an apparent *metal-insulator transition* in *both* mechanisms. For large R or ξ, the conductivity is finite *even* at very low temperatures, although the conductivity in both cases vanishes at zero temperature. We call this region ''metallic region.''

As we will compare our model with the experimental results of Kuriyama, we will further add an assumption that the *number of paths weakly depends upon temperature*. Then we can write $\sigma_0(T)$ as

$$\sigma_0(T)=\sigma_0^{(0)}(1+\epsilon T), \quad (16)$$

where $\sigma_0^{(0)}$ and ϵ are constants.

Since there is *no* difference between σ^{Wigner} and σ^{Poisson} for large R and ξ, we will consider only σ^{Wigner} with the above new assumption. In other words, we will consider

$$\sigma_\epsilon^{\text{Wigner}}(T)=\sigma_0(T)\int dE_{\text{G}}D_{\text{level}}^{\text{Wigner}}(E_{\text{G}})\exp(-E_{\text{G}}/k_{\text{B}}T). \quad (17)$$

It should be noted that $\sigma_0(T)$ is given by Eq. (16).

Corresponding to Figs. 1 and 4 in Ref. 5, we can trace the TDC parametrized by the size of the granule shown in Fig. 3. For the experimental results of Kuriyama[5] on the TDC of the non-heat-treated (AS) ACF's, we substitute $R=2.45$ nm. For that of $T_{\text{HT}}=850\ ^\circ\text{C}$, R corresponds to 4.00 nm, for that of $T_{\text{HT}}=1000\,^\circ\text{C}$, R corresponds to 5.4 nm, and for that of $T_{\text{HT}}=1200\,^\circ\text{C}$, R corresponds to 30.0 nm. Further we have adopted $\epsilon=1/1500$ as it produces the best fit. We can then see from Fig. 2 that the behavior of the curves plotted for appropriately normalized $\sigma(T)$ vs T is also in good agreement with all the experimental results of Kuriyama of $\sigma(T)/\sigma(250\ \text{K})$ (cf. Figs. 1 and 4 in Ref. 5).

As we have shown above, our theoretical model reproduces the experimental results of the TDC for disordered carbons very well, including the ''metal-insulator transition.''

From the viewpoint of quantum chaos theory, it is important that we determine which distribution (Wigner or Poisson) governs the system, i.e., whether the system is chaotic or not.[2,3] In the case of small granules, our theory indicates that the system should obey the chaotic law: when the activation energy associated with the conductivity is governed by the Wigner distribution, the conductivity formula can reproduce the experimental results of the small granules $R < 10$ nm. We could not discriminate whether the system in the ''metallic'' region is chaotic or not.

Even though we could not identify the conduction mechanism of the ''metallic'' regime within the meaning of chaos theory, we showed that the apparent metal-insulator transition occurs and the proposed formula reproduces the experimental results not only qualitatively but also quantitatively within our theoretical framework proposed in Ref. 1. In other words, our model is consistent from the ''insulator'' regime (i.e., small granule radius) to the ''metallic'' regime (the large radius case $R > 10$ nm). Accordingly we believe that this finding is very important from the viewpoint of further studies of disordered system.

Finally we should comment on the metal-insulator transition: although in our theory the conductivity vanishes at zero temperature, the conductivity for a certain case such as R or $\xi \sim 30$ nm is finite even at very low temperatures. This implies that at nonzero temperature we are in the ''metallic regime.'' Our results mean that there exists a certain class of the phenomena resembling ''metal-insulator transitions,'' which are *not* actually metal-insulator transitions but are apparent ones as in our model. It is not easy to determine their nature by means of experiments because we cannot reach zero temperature. It is hoped that our theory will enhance the further study of the disordered system and metal-insulator transition and facilitate future experiments.

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