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## Possible limit of conductivity in heavily doped polyacetylene

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**Abstract.** On the basis of the one-dimensional electron gas model, we use the memory function formalism to calculate the conductivity limit in heavily doped polyacetylene set by longitudinal acoustic phonon scattering. We have found that the impurity ion scattering can be ignored for real doping concentrations. At room temperature the intrinsic conductivity is estimated to be about  $7 \times 10^5 \Omega^{-1} \text{cm}^{-1}$  which is greater than those of most conventional metals.

### 1. Introduction

There has been considerable theoretical and experimental interest in the transport properties of polyacetylene in recent years. This is because its electrical conductivity can be quite changed when it is doped with impurities and a new concept of soliton excitation in it has been proposed to explain many experimental facts. For example, in the region of impurity concentration  $y < 0.001$ , polyacetylene is an insulator or semiconductor, but for the regime  $0.001 < y < 0.06$  its conductivity  $\sigma$  can be rapidly varied by more than 12 orders of magnitude on chemical or electrochemical doping and finally, when  $y > 0.06$ , it becomes a metal for which relatively simple and traditional metallic behaviour is observed. Recently in [1] a fine technique was developed to synthesise polyacetylene with a smaller number of  $sp^3$  defects than in polyacetylene made by other methods. A reduced number of  $sp^3$  defects implies a more perfect chain with longer average conjugation lengths. The improvements in synthesis and orientation have led to an electrical conductivity in the heavily doped sample of greater than  $1.5 \times 10^5 \Omega^{-1} \text{cm}^{-1}$ , which is close to the value for copper! However, the absence of a metallic temperature dependence indicates that the conductivity could be significantly raised by material perfection, and finally its value could be greater than that of copper. Therefore, it is of great interest to determine the possible limit on the intrinsic conductivity of heavily doped polyacetylene set by phonon and impurity scattering.

To date there is no unified mechanism to explain the transport properties for all doping regimes. At very low doping levels ( $y < 0.1\%$ ) the soliton band created by doping in the gap would be all filled (for donors). So, there are no free mobile charged carriers in the sample. In this regime the conductivity arises from the inter-soliton hopping of

electrons assisted by a few mobile neutral solitons as proposed in [2]. As to the transport in the intermediate-doping regime, although a number of different models have been proposed, it seems that no one has been able to explain the coexistence of both the high  $\sigma$  and the low Pauli susceptibility in this region successfully. Of the various models the variable-range hopping mechanism [3] and the Mott-type many-body effect mechanism [4] are the most promising. When  $y > 0.06$ , it is called a heavily doped regime in which metallic behaviour has been observed, but there is also considerable evidence that dimerisation or an energy gap persists into this high-doping regime [5]. There are also several theories for this regime [6, 7]. Unfortunately, however, it seems that this metallic polyacetylene is not yet understood.

In this paper, on the basis of the one-dimensional electron gas model we use the memory function formalism [8] to investigate the intrinsic conductivity limit set by only longitudinal acoustic phonon scattering. It is well known that this formalism has been successfully used to discuss the transport properties of electron gas, including the one- and two-dimensional transport problems.

In § 2, we present the model Hamiltonian of a quasi-one-dimensional conductor for the problem and the memory function method, and in § 3 we calculate the electron-phonon scattering rate. In § 4 we investigate the impurity ion scattering and find that it is ineffective in scattering conduction electrons. The impurities have two kinds of effect on the conductivity of doped polyacetylene. On the one hand, donor (acceptor) impurities give up electrons (holes) to the polyacetylene chains and create soliton levels in the gap. In the heavily doped regime, the energy gap is much reduced and the levels spread well across the gap [9]. The increase in charged carriers and decrease in the energy gap with increase in impurity concentration undoubtedly cause an increase in conductivity in this regime. On the other hand, impurity ions can scatter the conduction electrons (or holes) and so decrease the conductivity but, in a quasi-one-dimensional conductor such as polyacetylene chains, most dopant ions are not on the chains, i.e. not on the quasi-one-dimensional conduction path. Therefore the effective back-scattering is much reduced. In addition, owing to the quasi-one-dimensional nature of the charged transport in the doped polyacetylene, only the  $2k_F$  Fourier component of scattering potential is important. So, the effect on conductivity from impurity ion scattering is further reduced, and in fact can be ignored for a real doping concentration compared with the electron-phonon scattering. Finally, in § 5, we summarise the main points of the present paper and discuss them briefly.

## 2. Model Hamiltonian

The heavily doped polyacetylene can in many ways be thought of as a simple anisotropic metal. For example, its  $\sigma_{\parallel}$  is close to metal value [10] and it has a metal-like Pauli spin susceptibility [11]. The linear temperature dependence of its thermopower also indicates the metal-like behaviour [12]. Optical infrared and electron energy loss experiments support the absence of an energy gap in the heavily doped regime [13]. Although persistence of the doping-induced infrared absorption lines to a higher value of  $\langle y \rangle$  [14] shows non-uniformity of charge density along the chains and indicates oversimplification of the simple metal picture, we think that at least to a first approximation the heavily doped polyacetylene chains can be treated as a simple anisotropic metal picture.

In this work, we consider the polyacetylene as being composed of many parallel infinite long chains with a spacing of about 4 Å. Since the transverse hopping matrix

element  $t_{\perp}$  is much less than the longitudinal hopping matrix element  $t_{\parallel}$  ( $t_{\perp}/t_{\parallel} \approx 0.03$ ), the coupling between different chains is rather weak and usually can be ignored, especially when we are concerned only with the problem of the maximum conductivity reached in the heavily doped sample. So, the system can be approximately thought of as a quasi-one-dimensional conductor. However, we have to emphasise that the inter-chain coupling is necessary to avoid one-dimensional localisation caused by disorder of the impurities. Recently in [15] this problem was discussed in detail and a criterion was given such that  $L/a \gg 2t_{\parallel}/t_{\perp}$ , where  $L$  is the distance between chain breaks and  $a$  is the projection of the carbon-carbon distance along the chain direction. So long as the inequality is satisfied, the one-dimensional localisation due to any disorder can be avoided, and the conductivity is limited by  $L$  and by the phonon scattering.

Because the  $\pi$ -electron band width is about  $4t_0 \approx 10$  eV, we adopt the free-electron approximation for the band structure with  $\varepsilon_k = k^2/2m$ , which is more appropriate to the heavily doped region than to the tight-binding model. Since the number of thermally excited optical phonons at room temperature is small, these phonons are not expected to play an important role in scattering conduction electrons. So in this paper we shall consider only the acoustic phonon branch.

Finally we completely neglect the Coulomb interaction between electrons. This implies that we do not think the collective excitations due to many-body effect have a large effect on the transport properties in conducting polymers, and only single-particle theory is used in this paper.

We choose the Hamiltonian to be as follows:

$$H = \sum_{k,\sigma} \varepsilon_k c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_q h\omega_q b_q^{\dagger} b_q + \sum_{k,q,\sigma,i} u(q) \exp(i\mathbf{q} \cdot \mathbf{R}_i) c_{k+q,\sigma}^{\dagger} c_{k\sigma} + \sum_{k,q,\sigma} D(q) c_{k+q,\sigma}^{\dagger} c_{k\sigma} (b_q + b_{-q}^{\dagger}) \quad (1)$$

where  $c_{k\sigma}^{\dagger}$  and  $c_{k\sigma}$  are the electron creation and annihilation operators,  $b_q^{\dagger}$  and  $b_q$  are the phonon creation and annihilation operators with electron momentum  $\mathbf{k}$ , spin  $\sigma$  and phonon wavevector  $\mathbf{q}$ .  $u(q)$  is the impurity scattering potential, and  $D(q)$  is the interaction matrix element of electrons with the longitudinal acoustic phonons. The phonon frequency is represented by the Debye model,  $\omega_q = v_s q$ , with  $v_s$  the velocity of sound.

Let us briefly review the procedure for obtaining the DC conductivity from the standard memory function approach [8]. It has been pointed out [16] that the memory function method or force-balance approach is appropriate under isothermal conditions, while the Boltzmann equation or Kubo formula is valid under adiabatic conditions. However, for a typical metal where the chemical potential of electrons is usually much larger than temperature ( $\mu \gg T$ ), the isothermal and adiabatic resistivities obtained from two methods agree with each other.

It is well known that the dynamic conductivity deduced from the current-current correlation function can be written as [17]

$$\sigma(\omega) = (ine^2/m\omega)[1 + M(\omega)/\omega] \quad (2)$$

where  $n$  is the electron density,  $m$  is the electron mass and  $M(\omega)$  is the memory function.

Since we choose the free-electron model to describe our system, the Drude formula for conductivity can be used:

$$\sigma(\omega) = i(ne^2/m)[\omega + i/\tau(\omega)]^{-1} \quad (3)$$

where  $\tau(\omega)$  is the relaxation time function. In the high-frequency limit, equation (3) reduces to

$$\sigma(\omega) = (ine^2/m\omega)[1 - i/\omega\tau(\omega)]. \quad (4)$$

Comparing (4) with (2), one obtains [17]

$$1/\tau(\omega) = iM(\omega). \quad (5)$$

In general,  $M(\omega) = M_1(\omega) + iM_2(\omega)$  is a complex function with  $M_1(\omega)$  and  $M_2(\omega)$  as real functions. Taking the limit  $\omega \rightarrow 0$ , we obtain  $1/\tau(0) = -M_2(0)$  with  $M_1(0) = 0$  so that equation (3) becomes

$$\sigma(0) = ne^2\tau(0)/m = -ne^2/mM_2(0) \quad (6)$$

which is the expression for the DC conductivity or the inverse resistivity  $1/\rho$ . The expression for  $M_2(0)$  can be derived as the linear limit of a frequency-dependent generalisation of the balance equation [18]. It can be written as the sum of two terms  $M_2(0) = M_2^i(0) + M_2^{\text{ph}}(0)$ , with  $M_2^i(0)$  and  $M_2^{\text{ph}}(0)$  being the impurity contribution and phonon contribution respectively, to the memory function:

$$M_2^i(0) = \frac{y}{m} \sum_q |u(q)|^2 q_x^2 \left( \frac{d\Pi_2(q, z)}{dz} \right)_{z=0} \quad (7)$$

$$M_2^{\text{ph}}(0) = \frac{2}{NmT} \sum_q |D(q)|^2 q_x^2 \Pi_2(q, \omega_q) n(\omega_q) [1 + n(\omega_q)] \quad (8)$$

where  $y$  is the impurity concentration and  $N$  is the number of CH units per chain.  $q_x$  is the component of phonon momentum along the electric field direction, and  $n(\omega_q) = 1/[\exp(\omega_q/T) - 1]$  is the phonon distribution function.  $\Pi_2(q, z)$  denotes the imaginary part of the electron density-density retarded correlation function. When the electron-electron interaction is neglected, the expression for  $\Pi_2(q, z)$  is

$$\Pi_2(q, z) = 2\pi \sum_k [f(\varepsilon_k) - f(\varepsilon_{k+q})] \delta(z - \varepsilon_k + \varepsilon_{k+q}) \quad (9)$$

where  $f(\varepsilon_k)$  is the usual Fermi function. For the one-dimensional case it is easy to calculate  $\Pi_2(q, z)$  by replacing the summation over  $k$  by the integration

$$\begin{aligned} \Pi_2(q, z) &= L \int_{-\infty}^{\infty} dk f(\varepsilon_k) [\delta(z - \varepsilon_k + \varepsilon_{k+q}) - \delta(z + \varepsilon_k - \varepsilon_{k+q})] \\ &= \frac{2mL}{q} \left[ f\left(\frac{(q/2 + mz/q)^2}{2m}\right) - f\left(\frac{(q/2 - mz/q)^2}{2m}\right) \right] \end{aligned} \quad (10)$$

where  $L$  is the length of the one-dimensional chain.

### 3. The intrinsic conductivity

In this section we first take account of the resistivity due to the phonon scattering and leave the effect of the impurity scattering to the next section. Substituting equations (10) into (8), and replacing  $\Sigma_q$  by  $\int dq (L/2\pi)$ , we have

$$M_2^{\text{ph}}(0) = \frac{2L^2}{\pi NT} \int_0^{q_D} dq |D(q)|^2 qn(v_s q)[1 + n(v_s q)] \\ \times \left[ f\left(\frac{(q/2 + mv_s)^2}{2m}\right) - f\left(\frac{(q/2 - mv_s)^2}{2m}\right) \right]. \quad (11)$$

Since  $\mu \gg T$ ,  $f(x)$  can be approximately represented by  $\theta(\mu - x)$ ; here  $\theta(x)$  is the usual step function, and equation (11) then reduces to

$$M_2^{\text{ph}}(0) = -\frac{2L^2}{\pi NT} \int_{2(k_F - mv_s)}^{2(k_F + mv_s)} dq |D(q)|^2 qn(v_s q)[1 + n(v_s q)]. \quad (12)$$

For  $k_F \gg mv_s$  or  $v_F \gg v_s$ , the integral above can be approximately evaluated by means of the middle value theorem of integral, yielding

$$M_2^{\text{ph}}(0) = -(8m\omega_0 L^2 / \pi NT) |D(2k_F)|^2 \exp(\omega_0/T) [\exp(\omega_0/T) - 1]^{-2} \quad (13)$$

with  $\omega_0 = 2k_F v_s$ . Therefore, from (6) we finally obtain the following expression for the DC conductivity for our system:

$$\sigma(0) = (ne^2/m)(\pi NT/2m\omega_0 L^2) |D(2k_F)|^{-2} \sinh^2(\omega_0/2T). \quad (14)$$

We wish to discuss the temperature dependences of  $\sigma(0)$  for two limited cases. In the limit  $\omega_0 \gg T$ , we have

$$\sigma(0) = (ne^2 \pi / 8m^2 \omega_0)(N/L^2) |D(2k_F)|^{-2} T \exp(\omega_0/T). \quad (15)$$

Oppositely, when  $\omega_0 \ll T$ , equation (14) becomes

$$\sigma(0) = (ne^2/m)(\pi N/8mL^2) |D(2k_F)|^{-2} (\omega_0/T). \quad (16)$$

For heavily doped polyacetylene,  $\hbar\omega_0 \approx 0.12$  eV, which is obviously much larger than  $k_B T$  at room temperature. So, equation (15) for  $\sigma(0)$  should be suitable for our system. The electron-phonon scattering matrix element  $D(2k_F)$  can be found directly from the Su-Schrieffer-Heeger (SSH) Hamiltonian.

$$D(2k_F) = -i4\alpha(2NM\omega_0)^{-1/2} \quad (17)$$

where  $M$  is the CH unit mass, and  $\alpha$  is the electron-phonon coupling constant in the SSH Hamiltonian [19]. In the present free-electron model, we have  $\hbar^2 k_F^2 / 2m = \mu = 2t_0$ , where  $t_0$  is the  $\pi$ -electron hopping matrix element in the tight-binding approximation and  $k_F = \pi/2a$ . It then follows that  $m = \hbar^2 \pi^2 / 16t_0 a^2$ . Substituting (17) into (15) and inserting the Planck constant  $\hbar$  and the Boltzmann constant  $k_B$  when necessary (which are omitted in the previous equations for simplicity), we have

$$\sigma(0) = (4e^2 / \hbar \pi^3 a)(na^3)(M\omega_0 t_0^2 / \hbar \alpha^2)(k_B T / \hbar \omega_0) \exp(\hbar \omega_0 / k_B T). \quad (18)$$

In deriving (18) we have used the relation  $L/N = a$ . Equation (18) is similar to the result obtained previously in [20] using the Boltzmann equation but differs from the result in [15] by a factor of  $(k_B T / \hbar \omega_0)$ . We consider that this factor is necessary; otherwise, when

the temperature increases to  $k_B T \gg \hbar\omega_0$ , we shall not be able to obtain the linear  $T$  dependence of the metal-like resistivity but instead get an incorrect dependence  $\rho \propto T^2$ .

We adopt the following parameters in (18):  $a = 1.23 \text{ \AA}$ ,  $n = 4.5 \times 10^{22} \text{ cm}^{-3}$ ,  $\hbar\omega = 0.12 \text{ eV}$ ,  $t_0 = 2.5 \text{ eV}$  and  $\alpha = 4.1 \text{ eV \AA}^{-1}$ . At room temperature  $T = 300 \text{ K}$ , we estimate that  $\sigma(0) \approx 7 \times 10^5 \text{ \Omega}^{-1} \text{ cm}^{-1}$  which can be regarded as the maximum value of  $\sigma(0)$  for heavily doped polyacetylene.

#### 4. Resistivity due to impurity scattering

We now turn to the effect of impurity scattering on the resistivity. In the previous section we have given equation (10) for  $\Pi_2(q, z)$  from which it is easy to evaluate its derivative as

$$[d\Pi_2(q, z)/dz]_{z=0} = - (2mL/q)f(q^2/8m)[1 - f(q^2/8m)]. \quad (19)$$

Within the experimental temperature range  $T \ll \mu$ , the factor  $f(q^2/8m)[1 - f(q^2/8m)]$  is approximately a  $\delta$ -function:  $\delta(q^2/8m - \mu)$ . Thus, from (7) we obtain the memory function due to impurity scattering:

$$M_2^i(0) = - (8ymL^2/\pi)|u(2k_F)|^2 \quad (20)$$

and, finally, the corresponding resistivity is

$$\rho_i = - mM_2^i(0)/ne^2$$

or

$$\rho_i = 8yL^2(m/ne^2)[m|u(2k_F)|^2/\pi\hbar^3] \quad (21)$$

if the Planck constants are inserted when necessary. Following [15], the  $2k_F$ -component of the impurity scattering potential is taken to be of the following form:

$$|u(2k_F)|^2 = 4(e^2/\varepsilon_0 L)^2(a/\tilde{b}) \exp(-2\pi\tilde{b}/a) \quad (22)$$

where  $\tilde{b} = b(\varepsilon_{\parallel}/\varepsilon_0)^{1/2}$ , with  $b$  the distance of the impurity ion from the chain, and  $\varepsilon_{\parallel}$  and  $\varepsilon_0$  the dielectric constants parallel and perpendicular, respectively, to the chain. Finally, we obtain

$$\rho_i = 32y(m/ne^2)[m(e^2/\varepsilon_0)^2/\pi\hbar^3](a/\tilde{b}) \exp(-2\pi\tilde{b}/a). \quad (23)$$

For a minimum  $\tilde{b}/a \approx 2$ ,  $\varepsilon_0 = 2$  and  $y = 0.15$ , from (23) we estimate  $\rho_i \approx 3 \times 10^{-9} \text{ \Omega cm}$  which is much smaller than  $\rho_{\text{ph}}$ . If the anisotropic screening effect is included,  $\rho_i$  will be further reduced.

#### 5. Discussion and summary

In this paper we have found the possible limit of the conductivity in heavily doped polyacetylene under a very simple model using the memory function formalism. We have shown that the limit should be mainly set by the electron-phonon interaction, and the scattering from impurity ions has only a little effect on it. However, it does not rule out the possibility that some localised defects (e.g. chain ends and cross links) could have a large effect on the intrinsic conductivity. This kind of defect is not included in this work, and this important problem is left to a future discussion.

Using (18) and a set of chosen parameters used in the SSH model, we obtain the intrinsic conductivity at room temperature which is less than the value obtained in [15]. It is because in [15] the dependence of the electron-phonon scattering matrix elements and  $\omega_0$  on the magnitude of  $k$  away from  $\pm k_F$  was completely ignored. So, a formula of DC conductivity was derived in [15] which is similar to our equation (18), but without the factor  $k_B T / \hbar \omega_0$  (which equals approximately 0.2, for  $\hbar \omega_0 \approx 0.12$  eV at room temperature). Therefore, we think that the results in [15] overestimate the intrinsic conductivity of heavily doped polyacetylene. Even so, there is still good reason to say that the conductivity of heavily doped polyacetylene could be higher than that of conventional metals including copper.

In addition, it can be seen from (18) that we should make new conducting polymers with a higher molecular weight and frequency  $\omega_0$  to attain a higher conductivity than that of heavily doped polyacetylene.

Finally, we should mention that our method can include the interaction between electrons, if future experiments demonstrate the importance of many-body effects. Our theory is also applicable to other quasi-one-dimensional systems and is not restricted only to the conducting polymer.

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