Resistivity of metallic fullerenes: is there a lower limit to the mean free path ?

O. Gunnarsson and J.E. Han

The electrical resistivity ρ of a metal is usually interpreted in terms of a mean free path l, i. e., the average distance an electron travels before it is scattered. As the temperature T is raised, ρ is increased and l is reduced. In this semiclassical picture, however, l cannot become (much) shorter than the distance d between two atoms. The resistivity should then saturate at a value corresponding to $l \sim d$. This has been confirmed for many systems and was considered a universal behavior. Recently, a few apparent exceptions were found, e. g., alkali-doped fullerenes and high-temperature superconductors. These systems could, however, be in exotic states where only a small fraction of the conduction electrons contribute to the conductivity, and $l > d$ could then still be satisfied. It is therefore interesting to ask if there is some general principle, limiting the resistivity of a metallic system at large T. To address this problem, we have constructed a model of $\mathrm{A_3C_{60}}$, where the electrons are scattered by intramolecular vibrations. For this model we have performed an essentially exact calculation of the resistivity, using a quantum Monte Carlo (QMC) method.

The conduction in $\mathrm{A_3C_{60}}$ takes place in a partly filled $\mathrm{t_{1u}}$ band. The T-dependent part of the resistivity is assumed to be due to scattering against phonons with $\mathrm{H_g}$ symmetry. We therefore consider a model with a threefold degenerate $\mathrm{t_{1u}}$ level and a fivefold degenerate $\mathrm{H_g}$ Jahn-Teller phonon on each molecule, the hopping between the molecules and the coupling between the electrons and the phonons. The hopping takes into account that there is an orientational disorder of the molecules.

We have performed a finite temperature calculation, using a determinantal QMC method. The current-current correlation function is calculated for imaginary times and a transformation to real frequencies is made, using a maximum entropy method. This gives the optical conductivity and the resistivity. The QMC method has no 'sign-problem', and the resistivity of the model can be calculated essentially exactly down to quite small T.

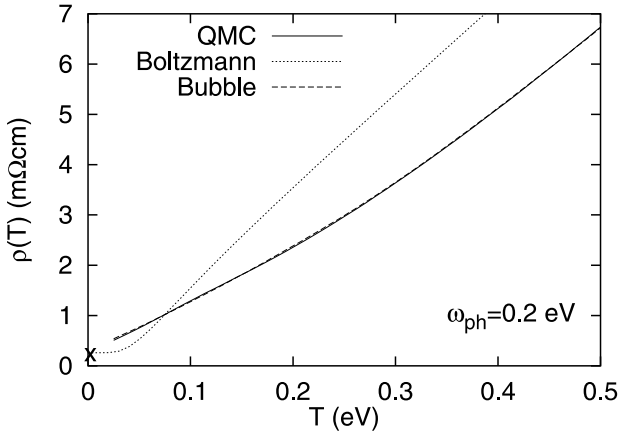

Figure 1: *The resistivity as a function of T according to the full QMC calculation, the Boltzmann equation (Bloch-Grüneisen) and the bubble diagram. The symbol $\times$ shows the $\rho(T=0)$ due to the orientational disorder. The figure illustrates that ρ can become extremely large, that the bubble calculation is quite accurate and that there is no qualitative break-down of the Boltzmann equation at high temperatures.*

Figure 1 shows the resistivity for a cluster of 48 $\mathrm{C_{60}}$ molecules with the dimensionless electron-phonon coupling constant $\lambda = 0.53$ and the phonon frequency $\omega_{ph} = 0.2$ eV. The QMC calculation (full line) shows that the resistivity can become very large, corresponding to $l \sim 0.7$ Å at $T = 0.5$ eV.

This should be compared with the separation $d = 10$ Å between two C_{60} molecules, i. e., $l \ll d$. By considering also unrealistically large temperatures, we emphasize the lack of a general principle of the type $l \gtrsim d$.

To interpret these results we have used a diagrammatic approach. In the Kubo formalism this requires the calculation of a bubble diagram including vertex corrections (see Fig. 2a)). We have neglected the vertex and calculated the bubble diagram using the electron Green's function from the QMC calculation. The resulting resistivity (dashed line in Fig. 1) is practically identical to the QMC result, justifying the neglect of vertex corrections for the present model. It was shown by Holstein that in the limit of a broad electronic band, all vertex corrections except ladder diagrams can be neglected and that a Boltzmann equation can be derived. Holstein's derivation is not strictly valid for the narrow band considered here (width ~ 0.6 eV), but our calculations show that his arguments are still qualitatively right. For our model with a $\mathbf{q}$-independent electron-phonon coupling, even the ladder diagrams can be neglected. Essentially following Holstein we obtain approximately a Boltzmann like conductivity

$$\sigma(T) \sim \int d\omega N(\omega) \left(-\frac{df(\omega)}{d\omega} \right) \frac{1}{\mathrm{Im}\Sigma(\omega)} \, |j_k|^2_{\varepsilon_k = \omega} \, , \tag{1}$$

where $N(\omega)$ is the density of states, f is the Fermi function, $\Sigma(\omega)$ is the electron self-energy, j_k is the current matrix element for a state with the label k and the energy ε_k. We interpret Im Σ as the inverse of the relaxation time. For a large T, Im Σ becomes comparable to or larger than the one-particle band width and the quasi-particle concept breaks down.

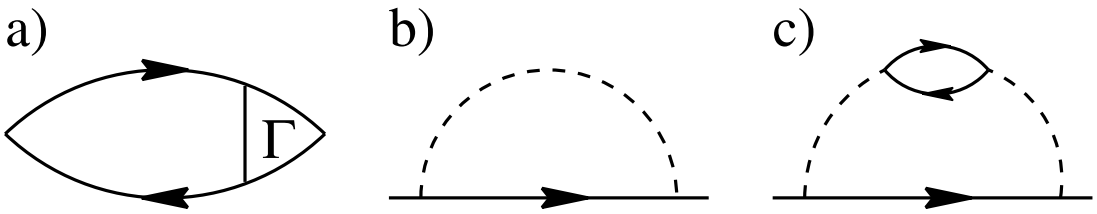

Figure 2: *Diagrams for the current-current response function a) and two approximations to the electron self-energy b) and c). The full and dashed lines represent electron and phonon Green's functions. Self-consistent Green's functions are used in a) but not in b) or c).*

The resistivity thus depends crucially on Σ. To understand its behavior, we considered the diagram in Fig. 2b) calculated with bare Green's functions and for simplicity neglecting the orbital degeneracy

$$\Sigma^{(1)}(\mathbf{k}, \omega) = g^2 \sum_{\mathbf{q}} \left[\frac{n_B(\omega_{ph}) + 1 - f(\varepsilon_{\mathbf{q}})}{\omega - \omega_{ph} - \varepsilon_{\mathbf{q}}} + \frac{n_B(\omega_{ph}) + f(\varepsilon_{\mathbf{q}})}{\omega + \omega_{ph} - \varepsilon_{\mathbf{q}}} \right] , \tag{2}$$

where g is the electron-phonon coupling constant and

$$n_B(\omega_{ph}) = \frac{1}{e^{\omega_{ph}/T} - 1} \quad \begin{array}{c} \longrightarrow \\ T \to \infty \end{array} \quad \frac{T}{\omega_{ph}} \tag{3}$$

is the Bose occupation number. For large T, the number of phonons $\mathrm{n_B}$ becomes large, leading to a large Im Σ, a small σ and a large ρ.

It is interesting to compare this with the resistivity due to the electron-electron scattering. Using the dynamical mean-field theory (DMFT) we have calculated the resistivity for a nondegenerate Hubbard model with the band width W and a simple cubic lattice with the lattice parameter a = 1 Å. We focused on the half-filled case, which is relevant for $\mathrm{A_3C_{60}}$, and we do not consider the case of a doped Mott insulator. Figure 3 shows $\rho(T)$ for different values of the on-site Coulomb interaction U. For $U < W$ the system is a metal and $\rho(T)$ grows with T, while for $U > W$ it is an insulator and $\rho(T)$ decreases with T. In the metallic case $\rho(T)$ saturates at $\rho \approx 0.4$ mΩ cm, which corresponds to $l/a \approx 1/3$. Thus, in contrast to the electron-phonon scattering case, electron-electron scattering does not lead to an l which is very much smaller than a in the metallic state of the half-filled Hubbard model.

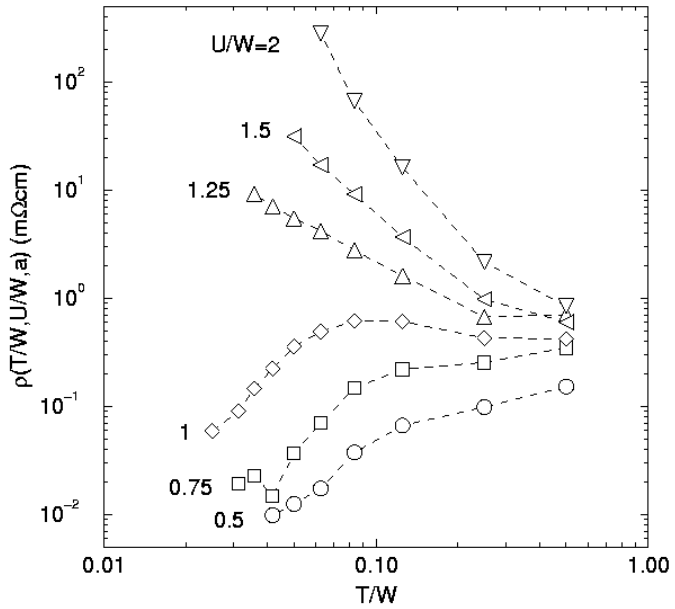

Figure 3: *The resistivity for the nondegenerate Hubbard model for different values of the Coulomb repulsion U. The figure illustrates how the resistivity saturates for large T in the electron-electron scattering case.*

To understand this, we have studied the electron self-energy Σ to second order in U, since Σ determines ρ in the DMFT. For low T, there is little scattering due to the small phase space available, as controlled by the Fermi functions. As T increases, the available phase space grows and ρ increases. However, for large T, ρ essentially saturates, since the Fermi functions approach a constant value. This is in strong contrast to the Bose occupation numbers (Eq.(3)), that increase with temperature. The qualitative difference between the two scattering mechanisms for large T can then be traced to the difference between fermions and bosons.

We have also addressed the validity of the Boltzmann equation for the case of the electron-phonon scattering in view of $l \ll d$. We have calculated the resistivity using the Ziman solution of the Boltzmann equation (Bloch-Grüneisen) and added the resistivity due to the orientational disorder as a T-independent contribution (dotted line in Fig. 1). Although the Boltzmann result is larger than the QMC result for large T, there is no qualitative break down of the Boltzmann equation even

when $l \ll d$. The justification for the Boltzmann equation in the limit $l \ll d$ is not the semi-classical derivation, but the (approximate) derivation from the full quantum mechanical Kubo formulation (Eq.(1)). The proper language in this limit is not in terms of a very short mean free path, but in terms of a very broad spectral function, as discussed above.

The QMC calculation gives an approximately linear T dependence. This agrees with the experimental result that ρ is linear down to about 100–200 K. The result may seem surprising, because at small T the probability of exciting finite energy phonons is exponentially small as is the contribution to ρ. Calculating the bubble diagram with the QMC electron Green's function also gives a linear behavior, while the use of a Green's function with the self-energy in Fig. 2b) gives an exponentially small contribution. The QMC Green's function also involves processes like in Fig. 2c), where a virtual phonon is created followed by the decay of this phonon into an electron-hole pair. The excitation energy of such a pair can be arbitrarily small, which leads to a ρ which is quadratic in T. In our model this goes over to an approximately linear behavior already for very small T.