Thermoelectric Coefficients for Electron Tunneling through a Nanocrystal

X. Zianni
Department of Applied Sciences,
Technological Educational Institution of Chalkida,
34 400 Psachna, Greece.
Email: xzianni@teihal.gr
Tel: 0030 22280 99541

Abstract

We discuss the behavior of the thermoelectric coefficients for electron tunneling through a nanocrystal. The distinct features of the conductance, the thermopower and the thermal conductance and the relation between them is discussed. In the quantum regime, the energy spectrum of the nanocrystal determines electron transport. Irregular energy spectrum results to non-periodic sequence of peaks paricularly pronounced in the thermal conductance. Quantum cofinement is responsible for the small vaues of the conductance and the thermal conductance. The effect of increasing thermal energy is condidered. The validity of Wiedermann-Franz law is discussed for energies ranging from the quantum regime up to the classical regime.

Motivation and Model

The thermoelectric phenomena of mesoscopic systems have been adequately studied in the ballistic and diffusive regime [1-3]. In the recent years, there have been proposed thermoelectric applications of quantum dot superlattices made of different material systems as well as periodic arrays of nanocrystals [4-10]. In all theoretical and experimental studies the crucial role of the values of the electrical and the thermal conductivities in these nanostructures has been pointed out. Reduced thermal conductivity has been found and has been attributed to electron and phonon confinement. So, these structures seem promising for efficient thermoelectric devices and this explains the noticeable growing research interest in their properties. Other device applications are also expected. Moreover, heating effects in nanodevices are crucial in determining their operation characteristics so that this field is the subject of current technological research.

The electron conductance, thermopower and thermal conductance of a quantum dot weakly coupled to two electrode leads has been calculated in the sequential tunneling regime within a linear response theory [11-13]. The Coulomb interaction has been treated within the framework of the 'orthodox model' for single-electron tunneling. It has been presented a systematic study of the electron transport coefficients for a wide range of values of the parameters that affect transport so that the effects of the charging energy, the thermal energy, the quantum confinement and the energy spectrum degeneracy become evident. Here, we give emphasis on our results on the effect of an irregular energy spectrum to the thermoelectric transport coefficients of nanocrystals.

We consider a nanocrystal (nc) weakly coupled to two electron reservoirs via tunnel barriers. Each reservoir is assumed to be in thermal equilibrium and there are a voltage difference V and a temperature difference ΔT between the two reservoirs. A continuum of electron states is assumed in the reservoirs that are occupied according to the Fermi-Dirac distribution. The Fermi energy, E_F, in the reservoirs is measured relative to the local conduction band bottom.

The nanocrystal is characterized by discrete energy levels E_p (p=1,2,..) that are measured from the bottom of the potential well. Each level can be occupied by either one or zero electrons. It is assumed that the energy spectrum does not change by the number of electrons in the nc. The states in the nc are assumed to be weakly coupled to the states in the electrodes so that the charge of the nc is well defined. We adopt the common assumption in the Coulomb blockade problems for the electrostatic energy $U(N)$ of the nc with charge Q=-Ne:

$$U(N) = (Ne)^2 / 2C - N\phi_{ext}, \qquad (1)$$

where C is the effective capacitance between the nc and the reservoirs and ϕ_{ext} is the contribution of external charges.

The tunneling rates through the left and right barriers from level p to the left and right reservoirs are denoted by Γ_p^l and Γ_p^r, respectively. It is assumed that energy relaxation rates for the electrons are fast enough with respect to the tunneling rates so that we can characterize the state of the nc by a set of occupation numbers, one for each energy level. It is also assumed that inelastic scattering takes place exclusively in the reservoirs not in the nc. The transport through the nc can be described by rate equations. Energy conservation is applied upon tunneling.

Due to the voltage difference V and the temperature difference ΔT between the two reservoirs, electric and thermal currents pass through the nc. In the regime of linear response, the current I and the heat flux Q are related to the applied voltage difference V and the temperature difference ΔT by the equations:

$$\begin{pmatrix} I \\ Q \end{pmatrix} = \begin{pmatrix} G & L \\ M & K \end{pmatrix} \begin{pmatrix} V \\ \Delta T \end{pmatrix}. \qquad (2)$$

The thermoelectric coefficients are related by Onsager relation that in the absence of a magnetic field is: M=-LT.

Equation (2) can be re-expressed with the current I rather than the voltage V as an independent variable:

$$\begin{pmatrix} V \\ Q \end{pmatrix} = \begin{pmatrix} R & S \\ \Pi & -\kappa \end{pmatrix} \begin{pmatrix} I \\ \Delta T \end{pmatrix} \tag{3}$$

The resistance R is the reciprocal of the isothermal conductance G. The thermopower S is defined as:

$$S \equiv -\left.\frac{V}{\Delta T}\right|_{I=0} = -L/G \tag{4}$$

The Peltier coefficient is defined as:

$$\Pi \equiv \left.\frac{Q}{I}\right|_{\Delta T=0} = M/G = ST \tag{5}$$

Finally, the thermal conductance is defined as:

$$\kappa \equiv -\left.\frac{Q}{\Delta T}\right|_{I=0} = -K\left(1+\frac{S^2GT}{K}\right). \tag{6}$$

The transport coefficients can be written [13] in the following general formalism:

$$\begin{aligned} G &= L^{(0)}, \\ S &= -\frac{1}{eT}(L^{(0)})^{-1}L^{(1)}, \\ K &= \frac{1}{e^2T}L^{(2)}. \end{aligned} \tag{7}$$

The electron thermal conductance, κ, is given by the expression:

$$\kappa = \frac{1}{e^2T}\left[L^{(2)} - L^{(1)}(L^{(0)})^{-1}L^{(1)}\right], \tag{8}$$

where

$$\begin{aligned} L^{(\alpha)} = \frac{e^2}{k_BT}\sum_{p=1}^{\infty}\sum_{N=1}^{\infty}\frac{\Gamma_p^l\Gamma_p^r}{\Gamma_p^l+\Gamma_p^r}P_{eq}(N)F_{eq}(E_p/N)\times \\ [E_p+U(N)-U(N-1)-E_F]^{(\alpha)}\times \\ \{1-f[Ep+U(N)-U(N-1)-E_F]\} \end{aligned} \tag{9}$$

Quantum regime

In this limit, the discrete energy spectrum determines transport properties of the nanocrystal. A single charging state contributes. For an equidistant energy levels spectrum ($E_p=p\Delta E$) and level-independent tunneling rates:

$$G = \frac{e^2}{k_BT}\gamma\frac{1}{4\cosh^2(\Delta/2k_BT)}, \tag{10}$$

$$S = -\frac{1}{eT}\left[-\frac{\Delta E}{2}Int\left(\frac{\Delta}{\Delta E}\right)+\Delta\right], \tag{11}$$

$$\kappa = k_B\gamma\left(\frac{\Delta E}{k_BT}\right)^2\frac{e^{-\Delta E/k_BT}}{1+4\cosh^2(\Delta/2k_BT)\,e^{-\Delta E/k_BT}}, \tag{12}$$

where $\gamma \equiv \Gamma^l\Gamma^r/(\Gamma^l+\Gamma^r)$.

The calculated conductance and thermopower are plotted in figures 1 and 2. It is seen that in the quantum limit periodic Coulomb-blockade oscillations are exhibited. The peaks of the conductance occur each time an extra electron enters in the nc. Both transport coefficients have the same periodicity:

$$\Delta E_F = \Delta E + e^2/C. \tag{13}$$

The sawtooth short-period oscillations of the thermopower are due to the discreteness of the energy spectrum.

In the thermal conductance behavior dominates the effect of quantum confinement due to the dependence on the ratio of the energy level spacing over the thermal energy, $\Delta E/k_BT$. This is analytically described by equation (12). The electron thermal conductance of nanocrystals decreases nearly exponentially with decreasing temperature. The dependence on the energy level separation, ΔE, in equation (12) shows an equally fast decrease as the size of the nanocrystal decreases. Hence, it is explicitly shown that quantum confinement is responsible for the fast decrease of the electron thermal conductance in the nanoscale. This behavior agrees with the observation that the thermal conductivity of nanocrystals is very small compared to that of bulk [e.g. 14].

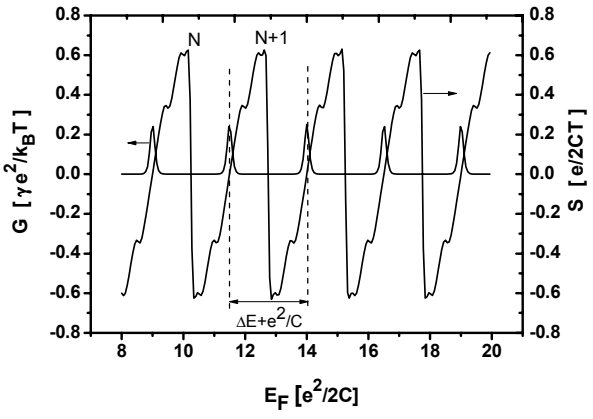

Fig. 1. Calculated conductance, G, and thermopower, S, for a series of equidistant energy levels with separation ΔE= 0.5 $e^2/2C$ and for k_BT=0.05 $e^2/2C$.

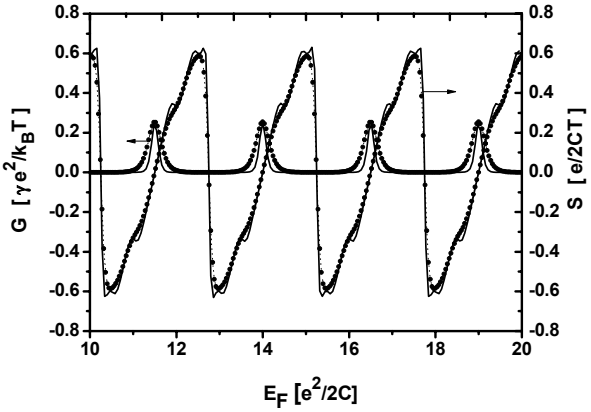

Fig. 2. As in figure 1 for two temperatures: k_BT=0.05 $e^2/2C$ (solid lines) and k_BT=0.1 $e^2/2C$ (dotted lines).

An equidistant energy level spectrum and energy independent tunneling rates have been assumed in equations (10-12). It is shown that: G_{max} decreases linearly with increasing thermal energy and it is nearly independent of the energy level spacing (figure 2); κ_{max} depends on both the thermal energy and the energy level spacing through their ratio, $\Delta E/k_BT$, and it decreases rapidly with decreasing temperature and increasing energy level spacing (figures 3 and 4). Let us now consider the effect of an irregular energy spectrum. This case is a more realistic approach for nanocrystals. Now, the conductance and the thermopower peaks will shift according the energy spectrum following locally equation (13) and will be therefore nonperiodic. The height of these peaks will be only weakly affected. The situation is different for the thermal conductance as predicted by equation (12). The position, but more considerably the shape and the height of the peaks of the thermal conductance are affected, resulting to a non-periodic sequence of peaks. This behavior is seen in figures (3) and (4) for two temperatures.

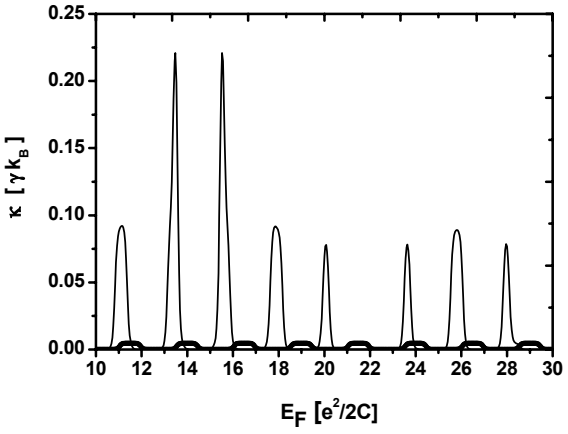

Fig. 3. Calculated thermal conductance, κ, for a series of equidistant levels with separation ΔE= 0.5 $e^2/2C$ (thick solid line) and for a irregular energy spectrum with the same density (solid line) for k_BT=0.05 $e^2/2C$.

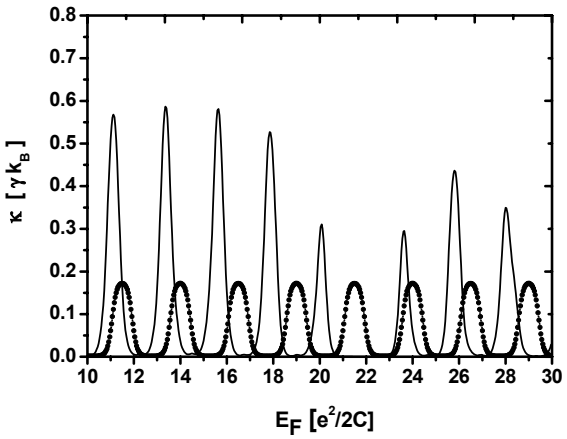

Fig. 4. As in figure 3, for k_BT=0.1 $e^2/2C$.

Classical regime

In the classical regime, the discreteness of the energy spectrum of the nc is screened by the thermal energy and the energy spectrum can be treated as a continuum. In this limit, the electron distribution function can be approximated by the Fermi-Dirac distribution. The probability distribution P takes the classical form $P_{eq}^{cl}(N)$.

For big charging energy, $e^2/C >> k_BT$, it is obtained:

$$G = \frac{e^2\rho}{k_BT}\gamma P_{eq}^{cl}(N)g(\Delta), \tag{14}$$

$$S = -\frac{1}{2eT}\Delta, \tag{15}$$

$$K = -\frac{\rho\gamma}{k_BT^2}\left[\frac{(\pi k_BT)^2 + \Delta^2}{3}\right]P_{eq}^{cl}(N)g(\Delta). \tag{16}$$

The electron thermal conductance is given by the equation:

$$\kappa = L_{CB}GT \tag{17}$$

$$L_{CB} = L_o\left[1 + \frac{1}{4\pi^2}\left(\frac{\Delta}{k_BT}\right)^2\right] \tag{18}$$

where $L_o = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2$ is the Lorentz number.

At low temperatures Coulomb blockade is exhibited. When the thermal energy becomes big compared with the charging energy, the amplitude of the Coulomb oscillations decreases and finally shrink. Wiedermann-Franz law holds in this limit.

At the peaks of the thermal conductance, equation (17) becomes: $\kappa = L_o GT$, i.e. Wiedermann-Franz law is valid. This is due to ballistic heat transfer at the peaks where the Coulomb barrier is suppressed. Away from the peaks it

holds: $L_{CB} > L_o$ and hence the heat transport is greater than the charge transport. The breakdown of the Wiedermann-Franz law is due to the Coulomb blockade effect. The maximum deviation from Wiedermann-Franz law is at the threshold of conduction and the deviation decreases as the conduction peak is approached, where the Coulomb barrier is suppressed. In the presence of the Coulomb barrier 'hot' electrons contribute to the conduction.

Finally, in order to examine the relation between the thermal conductance and the conductance, the ratio $\kappa_{\max} / L_o G_{\max} T$ is plotted versus the thermal energy in figure 5 for two cases of confinement: for $\Delta E = 0.1\ e^2/2C$ (dots) and for $\Delta E = 0.5\ e^2/2C$ (triangles). At low temperatures, quantum confinement that dominates over the thermal energy restricts the heat transport and the ratio is smaller than unity. Either in the quantum limit or in the intermediate region, quantum processes dominate in transport and cause deviations from Wiedermann-Franz law that is restored at the onset of the classical regime, at the peaks of conduction. Wiedermann-Franz law is expected to be restored faster with increasing temperature the weaker is the confinement. This is indeed found in the calculated data and it can be seen in figure 5 where the dots show a sharper increase than triangles with increasing thermal energy. Wiedermann-Franz law is again restored when due to thermal broadening all channels of conduction contribute equivalently to transport.

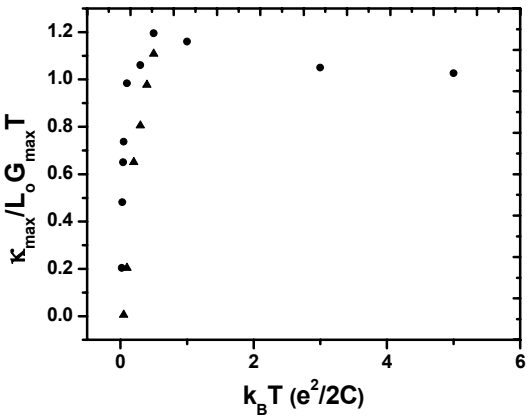

Fig. 5. The ratio $\kappa_{\max} / L_o G_{\max} T$ versus the thermal energy for two cases of confinement: for $\Delta E = 0.1\ e^2/2C$ (dots) and for $\Delta E = 0.5\ e^2/2C$ (triangles).

Conclusion

The thermoelectric transport coefficients for electron tunneling through nanocrystals show interesting dependence on the energy spectrum, the charging energy and the thermal energy. The interplay between the characteristic energies determines the transport behavior of a structure of nanocrystals. In the quantum regime, the signature of the energy spectrum in the thermoelectric properties has been shown to be particularly pronounced in the thermal conductance .

Acknowledgments

The present work has been co-funded by European Community funds and by National funds (E.P.E.A.E.K.) under the 'Archimides' programmme.

References

1. Butcher, P.N., Crystalline Semiconducting Materials and Devices , Plenum Press (New York, 1986).
2. Datta, S., Electronic Transport in Mesoscopic Systems, Cambridge University Press (Cambridge 1995).
3. Ferry, D.K., and Goodnick, S.M., Transport in Nanostructures, Cambridge University Press (Cambridge 1997).
4. Bao, Y., Liu, W.L., Shamsa, M., Alim, K., Balandin, A.A., Liu, J.L., Journal of the Electrochemical society Vol. 152 (2005), p. G432.
5. Vashaee, D., and Shakouri, A., Phys. Rev. Lett. Vol. 92 (2004), p. 106103.
6. Yang, R., and Chen, G., Phys. Rev. B Vol. 69 (2004), p. 195316 .
7. Balandin, AA., and Lazarenkova, O., Applied Physics Letters Vol. 82 (2003), p. 415.
8. Liu, J.L., Khitun, A., and Wang, K.L., Liu, W.L., Chen, G., Xie, Q.H., Thomas, S.G., Phys. Rev. B Vol. 67 (2003), p. 165333 .
9. Small, J. P., Perez, K. M., Kim, P., Physical Review Letters Vol 91 (2003), p. 256801.
10. Andreev, A.V., Matveev, K.A., Physical Review Letters Vol. 86 (2001), p. 280.
11. Beenakker, C.W.J., Phys. Rev. B Vol. 44 (1991), p. 1646.
12. Beenakker, C.W.J., and Staring, A.A.M., Phys. Rev. B Vol. 46 (1992), p. 9667.
13. Zianni, X., Phys.Rev. B Vol. 75 (2007), p. 045344.
14. Harman, T.C., Walsh, M.P., Laforge, B.E., Turner, G.W., Journal of Electronic Materials Vol 34 (2005), p. L19.