DE LA RECHERCHE À L'INDUSTRIE



THERMOELECTRIC CONVERSION IN DISORDERED NANOWIRES



Cosimo Gorini



Klaus Richter's group

Complex Quantum Systems, Universität Regensburg



www.cea.fr





Mainz, 28 / 01 / 2016



Thermoelectric effects: simultaneous charge & energy/heat flows

- The pioneers: Volta (1794), Seebeck (1821), Peltier (1834), Joule (1843), Thomson (1851; later Lord Kelvin).
- Theoretical formalisation: Onsager (1931).
- ☐ The golden age: ca. 1930 1960 (loffe).
- ☐ The rebirth: 1990's (Hicks & Dresselhaus).







Siberia can listen to Stalin's radio (USSR, 1948)



HOT

$$J_1 = L_{11}X_1 + L_{12}X_2$$
, $J_1 = \text{charge current}$
 $J_2 = L_{21}X_1 + L_{22}X_2$. $J_2 = \text{heat current}$
 $L_{ij} = \text{linear transport}$
 $COLD$

$$\begin{array}{ll} \text{Seebeck} \\ \text{(thermopower)} \quad S = -\left(\frac{\Delta V}{\Delta T}\right)_{J^e=0} = \frac{1}{eT}\frac{L_{12}}{L_{11}}, \quad \text{ Figure of merit } \quad ZT = \frac{L_{12}^2}{\det \mathbf{L}} \end{array}$$



Thermoelectricity : Rules of the game



Thermopower (or Seebeck coeff.):

$$S = -\left(\frac{\Delta V}{\Delta T}\right)_{J^e=0}$$

Maximize the efficiency i.e. the figure of merit :

$$ZT = \frac{GS^2}{K^e + K^{ph}}T$$

... keeping a reasonable electrical output power (power factor):

$$Q = GS^2$$

| PAGE 4

Why semiconductor nanowires?

"... a newly emerging field of low-dimensional thermoelectricity, enabled by materials nanoscience and nanotechnology"

Dresselhaus et al: Adv. Mater. 2007

"... fundamental scientific challenges could be overcome by deeper understanding of charge and heat transport"

Majumdar: Science 2004



SC nanowires



Reduced thermal conductance

Phonon vs electrons mean free path, geometrical designs (Hochbaum 2008, Heron 2010)

Enhanced thermopower

Field effect transistors (*Brovman 2013, Roddaro 2013* & many others)

Scalable output power

Arrays of parallel NWs (Pregl 2013, Stranz 2013)

DE LA RECHERCHE À L'INDUSTR



Some experimental realizations



Karg et al. (IBM Zurich), 2013



Shin et al. (Seoul), 2011



Hochbaum et al. (Berkeley CA), 2008

However \rightarrow Imbalance between experimental / theoretical works !

DE LA RECHERCHE À L'INDUSTRIE



Outline

Aller à l'idéal et comprendre le réel.

Jean Jaurès

Nanowires in the Field Effect Transistor configuration The 1D Anderson Model

- Thermopower of single NW: low T elastic regime
- □ Thermopower of single NW: inelastic phonon-assisted regime
- Parallel nanowires: scalable power factor and hot spot cooling
- □ 3-Terminal thermoelectric ratchet (``all-in-one thermocouple'')



DE LA RECHERCHE À L'INDUSTR



Field-Effect Transistors (FET)



Setup used by P. Kim (Columbia) (2013)

"Seebeck" configuration: thermal bias "Peltier" configuration: voltage bias



- **Substrate**: Electrically and thermally insulating
- Gate: «back» or «top»
- Heater: for thermoelectric measurements



 $\Pi = ST$: equivalent within linear response if time-reversal symmetry preserved (Kelvin relation)

Goal: effect of gate modulation on the thermopower



1D Anderson Model

Prototypical model of localized system



- 1D electronic lattice with on-site (uniform) disorder $V_i \in (-W/2, W/2)$
- Tight-binding Hamiltonian

$$\mathcal{H} = -t \sum_{i=1}^{N-1} \left(c_i^{\dagger} c_{i+1} + \text{h.c.} \right) + \sum_{i=1}^{N} (V_i + V_g) c_i^{\dagger} c_i$$

- All electrons are localized with localization length ξ (E)
- States distributed within an impurity band $2E_B \approx 4t+W$
- Behavior of the typical thermopower when the gate voltage V_g is varied

Analytical expressions derived in weak disorder limit

W=t : band edge at ~ 2t+W/2 ~ 2.5t 0.5 Density of states 0.4 > 0.3 0.2 0.1 -2 -1 Localization length इ 100 75 50 25 -2 -1 0 1 E

"Bulk" formulas:

$$\nu_b(E) = \frac{1}{2\pi t \sqrt{1 - (E/2t)^2}}$$

$$\xi_b(E) = \frac{24}{W^2} \left(4t^2 - E^2\right)$$

"Edge" formulas: $\nu_e(E) = \sqrt{\frac{2}{\pi}} \left(\frac{12}{tW^2}\right)^{1/3} \frac{\mathcal{I}_1(X)}{[\mathcal{I}_{-1}(X)]^2}$ $\xi_e(E) = 2 \left(\frac{12t^2}{W^2}\right)^{1/3} \frac{\mathcal{I}_{-1}(X)}{\mathcal{I}_1(X)}$ $\mathcal{I}_n(X) = \int_0^\infty y^{n/2} e^{-\frac{1}{6}y^3 + 2Xy} \, dy$ $X = (|E| - 2t)t^{1/3}(12/W^2)^{2/3}$

B. Derrida & E. Gardner, *J. Physique* 45, 1283 (1984)



Nanowires in the Field Effect Transistor configuration The 1D Anderson Model

Thermopower of single NW: low T elastic regime Thermopower of single NW: inelastic phonon-assisted regime Parallel Nanowires: scalable power factor and hot spot cooling 3-Terminal thermoelectric ratchet





Elastic regime: Thermopower

<u>Theory</u>: Transport mechanism: elastic (coherent) tunnelling

Localized regime: **7** decays exponentially with length

 $[\ln \mathcal{T}]_0(E) = -\frac{2N}{\xi(E)}$

Typical τ depends on the energy via $\xi(E)$ (localization length)

Low Temperatures + Linear Response \rightarrow Mott formula:

$$S \approx \frac{\pi^2}{3} \frac{k_B}{e} k_B T \left. \frac{\mathrm{d} \ln \mathcal{T}}{\mathrm{d} E} \right|_{\mu}$$

<u>Numerics</u>:

Recursive Green Function calculation of S

R. Bosisio, G. Fleury, & J.-L. Pichard, New J. Phys. 16:035004 (2014)





Enhancement of the thermopower at the band edges (role of $\xi(E)$)



Analytical description of the results

- Sommerfeld Expansion (low T) Wiedemann-Franz law \rightarrow Low S

Very low power factor $Q = GS^2$ because of the exponential reduction of G at the band edges

Interest: Ultra-low T Peltier cooling?

 $OR \rightarrow$ toward higher temperatures!





- Nanowires in the Field Effect Transistor configuration The 1D Anderson Model
- ✓ Thermopower of single NW: low T elastic regime
- □ Thermopower of single NW: inelastic phonon-assisted regime
- Parallel Nanowires: scalable power factor and hot spot cooling
- **3**-Terminal thermoelectric ratchet
- Conclusions and prospects

Variable Range Hopping: Transport Mechanism



Mott \rightarrow competition between tunneling and activated processes

$$G_{ij} \sim e^{-2|x_i - x_j|/\xi} e^{-(|E_i - \mu| + |E_j - \mu| + |E_i - E_j|)/2k_BT}$$

 L_M

Variable Range Hopping: phonon-assisted transport \rightarrow <u>sequence of hops</u> of variable size

Optimal hop size: *Mott hopping length*

or Mott hopping energy

$$L_{M} \simeq \left(\frac{\xi}{2\nu T}\right)^{1/2} \longrightarrow G \sim e^{-\frac{2L_{M}}{\xi}} = e^{-\frac{\Delta}{k_{B}T}}$$
$$\Delta = \left(\frac{2T}{\xi\nu}\right)^{1/2} \longrightarrow G \sim e^{-\frac{2L_{M}}{\xi}} = 15$$

DE LA RECHERCHE À L'INDUSTR

Transport Mechanisms



Inelastic (Phonon-Assisted) Regime: method

Essential ingredients to build & solve the Random Resistor Network

1. Transition rates (Fermi golden rule)





$$\Gamma_{i\alpha} = \gamma_{i\alpha} f_i \left[1 - f_\alpha(E_i) \right] \quad \alpha = 1$$

 $\gamma_{i\alpha} \simeq \gamma_e \exp(-2x_{i\alpha}/\xi_i)$

Between localized states [Inelastic hopping rates]

$$\Gamma_{ij} = \gamma_{ij} f_i (1 - f_j) [N_{ij} + \theta(E_i - E_j)]$$

$$\gamma_{ij} \simeq \gamma_{ep} \exp(-2x_{ij}(\xi)) \leftarrow \xi \text{ energy dependence usually neglected!}$$

$$\rightarrow \gamma_{ij} \propto |\langle \psi_i | \psi_j \rangle|^2 \simeq \gamma_{ep} \left| \frac{(1/\xi_j) \exp(-x_{ij}/\xi_i) - (1/\xi_i) \exp(-x_{ij}/\xi_j)}{(1/\xi_i - 1/\xi_j)} \right|^2$$

Miller & Abrahams, *PR* (1960), Ambegaokar, Halperin & Langer *PRB* (1971), Jiang, Entin-Wohlman & Imry., *PRB* (2014)

2. Fermi distributions at equilibrium (no bias)

$$f_i^0 = \left(e^{(E_i - \mu)/kT} + 1\right)^{-1} \quad f_\alpha = f_\alpha^0(E_i) = \left(e^{(E_i - \mu)/kT} + 1\right)^{-1}$$

3. Occupation probabilities out of equilibrium

$$f_i = f_i^0 + \delta f_i \qquad f_\alpha = f_\alpha^0 + \delta f_\alpha$$

4. Currents

$$I_{ij} = e \left(\Gamma_{ij} - \Gamma_{ji} \right) \qquad \qquad I_{i\alpha} = e \left(\Gamma_{i\alpha} - \Gamma_{\alpha i} \right)$$

5. Current conservation at every node i (Kirchoff) N coupled equations in N variables

$$\left(\sum_{j\neq i} I_{ij}\right) + I_{iL} + I_{iR} = 0 \qquad \Rightarrow \quad \delta f_i$$

Miller – Abrahams Resistor Network

6. Total particle/heat currents

Summing all terms flowing out from L(R) terminal

$$J_L^e = -\sum_i I_{iL} = \sum_i I_{iR},$$
$$J_{L(R)}^Q = \sum_i \left(\frac{E_i - \mu_{L(R)}}{e}\right) I_{L(R)i}.$$



(Having assumed Peltier configuration: T constant everywhere)

Jiang, Entin-Wohlman & Imry., PRB (2014)

DE LA RECHERCHE À L'INDUSTRIE

Inelastic Regime: Typical thermopower



- Thermopower enhancement when the band edges are approached
- Rich behaviour of the T-dependence of the thermopower, "reflecting" the shape of the density of states and localization length

| PAGE 20

R. Bosisio, C. Gorini, G. Fleury, & J.-L. Pichard, New J. Phys. 16:095005 (2014)

Inelastic regime: theory



Inelastic Regime: Typical thermopower



R. Bosisio, C. Gorini, G. Fleury, & J.-L. Pichard, New J. Phys. 16:095005 (2014)

DE LA RECHERCHE À L'INDUSTR

Inelastic Regime: Mott energy

$$S = \frac{\langle E - \mu \rangle}{eT} = \frac{1}{eT} \frac{\int dE \left(E - \mu \right) \nu(E) p(E)}{\int dE \nu(E) p(E)}$$

Integration inside $[\mu - \Delta, \mu + \Delta]$

Mott's Hopping Energy: finite range of states contributing to transport

$$\Delta = k_B \sqrt{TT_M} \propto \sqrt{\frac{T}{\xi\nu}} \gg k_B T$$



S depends on the asymmetry of the states around μ within [μ - Δ , μ + Δ]



- Nanowires in the Field Effect Transistor configuration The 1D Anderson Model
- ✓ Thermopower of single NW: low T elastic regime
- ✓ Thermopower of single NW: inelastic phonon-assisted regime
- Parallel Nanowires: scalable power factor and hot spot cooling
- **3**-Terminal thermoelectric ratchet
- Conclusions and prospects

Arrays of parallel nanowires



- Neglect *inter*-wire hopping \rightarrow independent nanowires
- Transport through each NW: VRH / NNH regime (same treatment as before)

DE LA RECHERCHE À L'INDUSTR

Parallel nanowires: power factor and figure of merit

 $G \approx M G_0$ $K^e \approx M K_0^e$ $S \approx S_0$

Scalable Power Factor

(without affecting the electronic figure of merit)

 $\mathcal{Q} = GS^2 \approx M G_0 S_0^2$



Parameters: $M = 150, W = t, \gamma_e = \gamma_{ep} = t, L = 450$ P~µW for 10⁵ NWs (1 cm) and δ T-10 K

R. Bosisio, C. Gorini, G. Fleury, & J.-L. Pichard, Phys. Rev. Applied 3, 054002 (2015)

Parallel nanowires: power factor and figure of merit

Estimation of the parasitic phononic contribution to ZT



(For doped Si-NWs and SiO₂ substrate)

DE LA RECHERCHE À L'INDUSTRI

Parallel nanowires: Hot Spot cooling

Hopping heat current through each localized state i

$$I_i^Q = \sum_j I_{ij}^Q = \sum_j (E_j - E_i) I_{ij}^N$$

E_i randomly distributed \rightarrow Local fluctuations

$$\mathcal{I}^Q_{x,y} = \sum\nolimits_{i \in \Lambda_{ph} \times \Lambda_{ph}(x,y)} I^Q_i$$

Λ_{ph}: inelastic phonon mean free path = thermalization length in the substrate



R. Bosisio, C. Gorini, G. Fleury, & J.-L. Pichard, Phys. Rev. Applied 3, 054002 (2015)

DE LA RECHERCHE À L'INDUSTRI

Parallel nanowires: Hot Spot cooling



Parameters: $M = 150, W = t, \gamma_e = \gamma_{ep} = t, k_B T = 0.25t, \Lambda_{ph} = 150a$ (Heat currents in unit of t^2/\hbar)

R. Bosisio, C. Gorini, G. Fleury, & J.-L. Pichard, Phys. Rev. Applied 3, 054002 (2015)



Opportunities for heat management in microstructures

E.g.: hot spot cooling in microelectronics: transferring heat some microns away



| PAGE 30



- Nanowires in the Field Effect Transistor configuration The 1D Anderson Model
- ✓ Thermopower of single NW: low T elastic regime
- ✓ Thermopower of single NW: inelastic phonon-assisted regime
- ✓ Parallel Nanowires: scalable power factor and hot spots cooling
- □ 3-Terminal thermoelectric ratchet
- **Conclusions and prospects**

3-Terminal thermoelectric ratchet



Simple (ideally Si – based)

Bosisio, Fleury, Pichard & Gorini, arXiv (2015)

| PAGE 32 Sànchez & Büttiker, *PRB* (2011) \rightarrow Low T, coherent, feasible but extremely low power

Heat Source

DE LA RECHERCHE À L'INDUSTRIE

3-Terminal thermoelectric ratchet

























The end

Aller à l'idéal et comprendre le réel.

Jean Jaurès

\Box Variable Range Hopping \rightarrow inelastic, large window for e-h asymmetry

 \Box Parallel nanowires \rightarrow high Seebeck AND good power factor Q

- Gate-controlled local heat exchanges (hot spots cooling)
- □ 3-Terminal thermoelectric ratchet:
 - 1. Simple setup, energy harvester/cooler
 - 2. Good power factor Q and electronic ZT (0.1 100)



Universität Regensburg







SFB 689

Riccardo Bosisio

Geneviève Fleury

Jean-Louis Pichard



The future

Wishlist

- Rigorous treatment of e-ph coupling
- Combining DFT calculations of γ_e and γ_{ep}
- Non-linear regime (higher output powers), multi-terminal setups
- Heat-to-spin conversion I: magnetism and/or spin-orbit in wires
- Heat-to-spin conversion II: hot magnon bath
- Time-dependent configurations.







DE LA RECHERCHE À L'INDUSTRI

Inelastic Regime: Thermopower fluctuations

Bulk of the band





R. Bosisio, C. Gorini, G. Fleury, & J.-L. Pichard, New J. Phys. 16:095005 (2014)

DE LA RECHERCHE À L'INDUSTRI

Parasitic Phonon Contribution to ZT

$$ZT = \frac{Z_e T}{1 + K^{ph}/K^e}$$
$$\frac{Z}{Z_e} = \left[1 + \frac{\kappa^{sub}\Sigma^{sub} + M\kappa_0^{nw}\Sigma^{nw}}{M\kappa_0^e\Sigma^{nw}}\right]^{-1}$$

 $\kappa_0^{nw} \approx 2 \,\mathrm{W/(K.m)}$ at $T \approx 100 \,\mathrm{K}$ $\kappa^{sub} \approx 0.7 \,\mathrm{W/(K.m)}$

(For doped Si-NWs and SiO₂ substrate)

DE LA RECHERCHE À L'INDUSTR

Parallel nanowires: addenda

DE LA RECHERCHE À L'INDUSTRI

Density of states with Coulomb gap

Thermopower Enhancement: experimental results

20

10

400

300

200

100

-60

(a)

(b)

-40

Z_{AC} = .01G

 $Z_{AC} = .1G$

Z_{AC} = 1G

Z_{DC} = .1G

-20

0

Gate voltage $V_{a}(V)$

ഗ

Cond. (JuS)

Thermopower (μ V/K)

Group of Philip Kim (preprint 2013) Similar data in the group of F. Giazotto or H. Riel

(Field effect transistor device configuration)

Largely enhanced thermopower near the band edge of the nanowire

(Experiments mainly carried out at Room Temperature)

20

40

T = 300K

Linear response: Onsager formalism

(Two-terminal) Coupled 1D charge and heat transport

Transport coefficients & Onsager matrix elements

$$G = \left(\frac{J^e}{\Delta V}\right)_{\Delta T=0} = \frac{e^2}{T}L_{11} \qquad S = -\left(\frac{\Delta V}{\Delta T}\right)_{J^e=0} = \frac{1}{eT}\frac{L_{12}}{L_{11}}$$
$$K = \left(\frac{J^Q}{\Delta T}\right)_{J^e=0} = \frac{1}{T^2}\frac{\det \mathbf{L}}{L_{11}} \qquad \Pi = \left(\frac{J^Q}{J^e}\right)_{\Delta T=0} = \frac{1}{e}\frac{L_{21}}{L_{11}}$$
PAGE 42

Elastic Regime: validity of Sommerfeld expansion

Q: Validity of the Mott's formula for S

Validity of Sommerfeld Expansion —

Wiedemann-Franz (WF) law, Mott's formula

| PAGE 43

Estimation for Si nanowire: ~100 mK

Elastic Regime: Typical thermopower of a tunnel barrier

In the basis $\{1, N, 2, ..., N - 2\}$ $G = [E - H - \Sigma_L - \Sigma_R]^{-1}$

$$G = \begin{pmatrix} A & B \\ \tilde{B} & C \end{pmatrix}^{-1} \qquad A = (E - V_g - \sigma)\mathbf{1}_2 \qquad \qquad \sigma = \text{nonvanishing} \\ \text{part of } \Sigma$$

$$\mathcal{T}(E) = \operatorname{Tr}\left[\begin{pmatrix} \gamma & 0\\ 0 & 0 \end{pmatrix} G_A \begin{pmatrix} 0 & 0\\ 0 & \gamma \end{pmatrix} G_A^{\dagger}\right] = \gamma^2 |G_A^{(1N)}|^2 \qquad \gamma = -2\operatorname{Im}(\sigma)$$

$$S = t \left. \frac{\mathrm{d}\ln \mathcal{T}}{\mathrm{d}E} \right|_{E_F}$$

$$\frac{S_0^{TB}}{N} \underset{N \to \infty}{\approx} \frac{1}{N} \frac{2t}{\Gamma(E_F)} \left. \frac{\mathrm{d}\Gamma}{\mathrm{d}E} \right|_{E_F} \pm \frac{1}{\sqrt{\left(\frac{E_F - V_g}{2t}\right)^2 - 1}}$$

| PAGE 44

DE LA RECHERCHE À L'INDUSTR

Three-terminal quantum thermal machines

Efficiency: depends on the sign of the heat currents

$$\eta_1 \equiv rac{\dot{W}}{J_1^Q} \qquad \qquad \eta_2 \equiv rac{\dot{W}}{J_2^Q}$$

Carnot limit

$$\eta_{C,1} = 1 - \frac{T_3}{T_1} + \frac{J_2^Q}{J_1^Q} (1 - \zeta_{32}) = \eta_C^{II} + \frac{J_2^Q}{J_1^Q} (1 - \zeta_{32})$$
$$\eta_{C,2} = \eta_C^{II} - \frac{T_3}{T_1} \left[\frac{J_1^Q}{J_2^Q} (1 - \zeta_{13}) - (1 - \zeta_{12}) \right]$$
$$\eta_{C,12} = 1 - \frac{T_3}{T_1} \left(1 + \frac{\zeta_{12} - 1}{1 + \frac{J_1^Q}{J_2^Q}} \right) = \eta_C^{II} - \frac{T_3}{T_1} \frac{\zeta_{12} - 1}{1 + \frac{J_1^Q}{J_2^Q}}$$

Not a function of the temperatures only !!

$$\eta = \frac{W}{\sum_{i_+} J_i^Q}$$
$$\eta_{12} \equiv \frac{\dot{W}}{J_1^Q + J_2^Q}$$

Efficiencies at maximum power

$$\eta_1(\dot{W}_{\max}) = \frac{\eta_{C,1}}{2} \frac{\mathcal{Z}_{11}T}{C_1 + \mathcal{Z}_{11}T}$$

$$\eta_2(\dot{W}_{\max}) = \frac{\eta_{C,2}}{2} \frac{Z_{22}T}{C_2 + Z_{22}T}$$
$$\eta_{12}(\dot{W}_{\max}) \simeq \frac{\eta_{C,12}}{2} \frac{Z_{12}T}{C_{12} + Z_{12}T}$$

Generalized figures of merit

$$\mathcal{Z}_{ij} = f(G_{kl}S_{mn}S_{pq}/K_{uv}) \quad k, l, m, n, u, v \in \{1, 2\}$$
$$C_{ij}, C_i = f(K_{ij}, X_1^T, X_2^T)$$

F. Mazza, R. Bosisio, G. Benenti, V. Giovannetti., R. Fazio & F. Taddei, New J. Phys. (2014)

DE LA RECHERCHE À L'INDUSTRI

GATE MODULATED CARRIER DENSITY

In *G*(*V* gate) at three temperatures in a large gate voltage range (details of the conductance pattern are not seen for this gate voltage sampling)Inset: the same curve in a linear scale. Note the linearity at voltages above the transition.

Edge of the impurity band = -2,5 V (Complete depletion of the disordered nanowire)

| PAGE 46

DE LA RECHERCHE À L'INDUSTR

CONDUCTANCE FLUCTUATION S INDUCED BY VARYING THE GATE VOLTAGE

