Thermoelectric Transport in Disordered and Nanosystems

(Patent Pending)

Yoseph Imry, Weizmann Institute

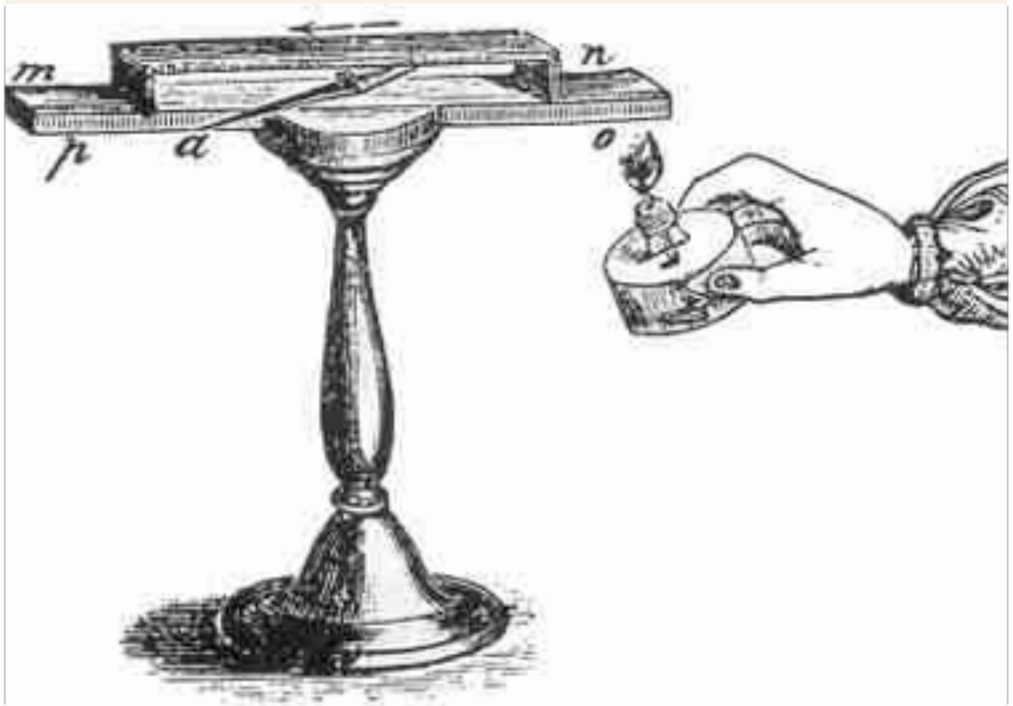
Based on:

Uri Sivan and YI, Phys Rev **B33**, 551 (1986) **[Landauer, M-I]**;

YI and A. Amir, in "50 Years of Anderson Localization" and ArXiv (2010) **[near Anderson transition]**

O. Entin-Wohlman, YI and A. Aharony, PRB 2010, and ArXiv **[molecular junctions].**

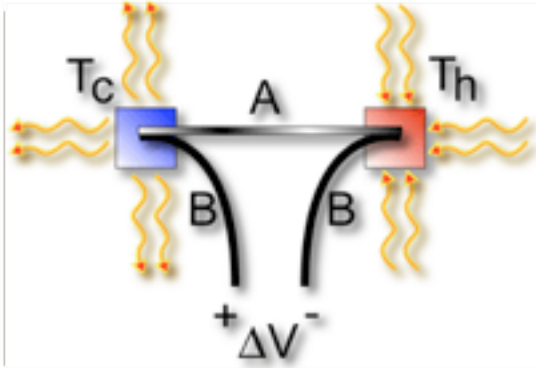
J-H Jiang, O. Entin-Wohlman and YI, PRB 2012 [molecular jcts, **hopping, nano**] and ArXiv; p-n junctions, submitted to PRB.



T. Seebeck-deflection of a compass needle (circa 1823)

G. Magnus

J. C. A. Peltier



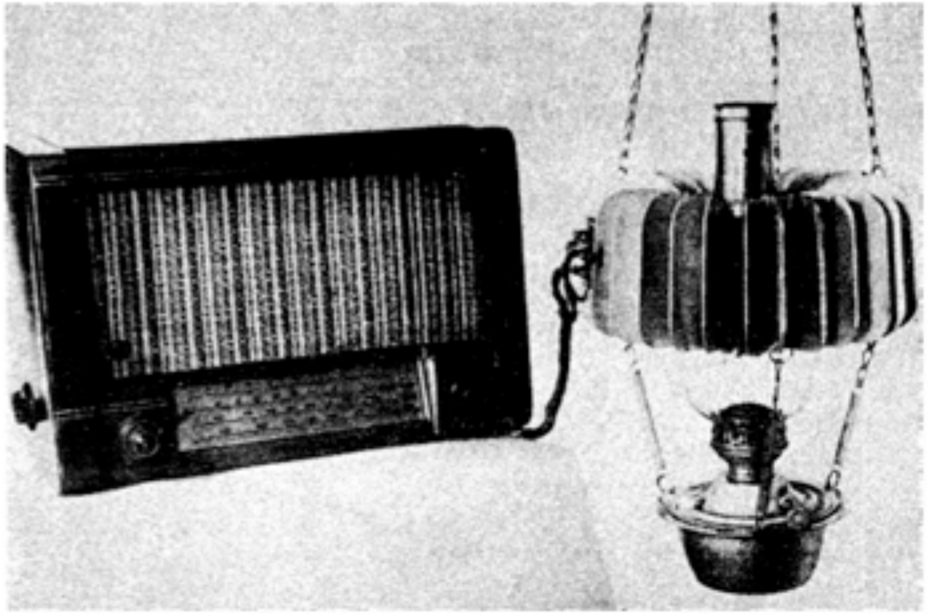
W. Thomson

(Lord Kelvin)

A. F. Ioffe

semiconductors

and figure of merit



Oil burning lamp powering a radio using the first commercial thermoelectric generator containing ZnSb built in USSR, circa 1948

OUTLINE

I. General Considerations.

II. Thermopower near the Anderson Transition.

III. Three (special) terminals thermoelectric transport in a vibrating molecular junction.

IV. Hopping thermopower in disordered two-site, and longer, chains, dominance of edges.

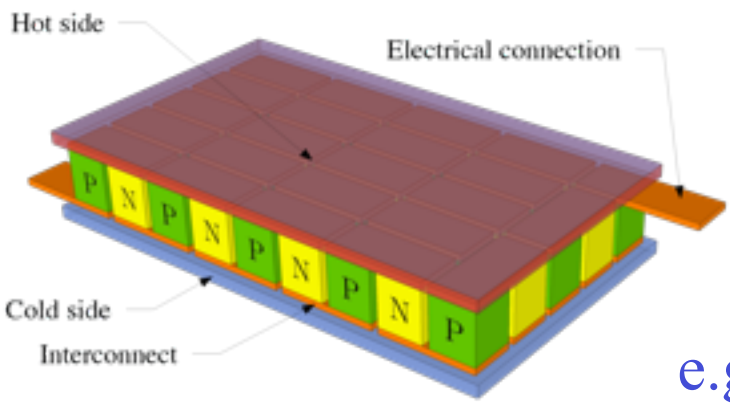
Long-Range Motivation:

Use understanding of CM physics to achieve:

LARGE THERMOELECTRIC EFFECTS

In the process: info on critical behavior around the Anderson transition, insights on 3-terminal and on hopping thermoelectricity.

Themoelectric energy conversion and manipulation, using "nondiagonal" (Onsager-type) transport to cool, convert heat to energy, etc.



$$\begin{pmatrix} I \\ I_Q \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} V \\ \Delta T \end{pmatrix},$$

e.g. Harman and Honig, Thermoelectric… McGraw-Hill (1967)

Can use the nondiagonals to convert heat to electricity, to make it flow "from cold to hot" terminals…

Need **large** thermopower and conductivity, **small** thermal conductivity.

Definitions and simple considerations

- Thermopower, S = voltage/temp difference (I=0).
- "Fig of merit", **ZT**

$$Z = S^2\sigma/K.$$

Best current values, **ZT ~3.**

- Good to increase S! and reduce K of phonons.
- Without phonons (best) , Wiedemann-Franz gives:

$$ZT = (3/\pi^2)\ s^2, \quad s = Sk_B/e$$

k_B/e = 85-86 μV/K, natural unit for thermopower

WF: $\sigma T/K = (3/\pi^2)\ (e/k_B)^2$, roughly valid (for e's) **often**.

Seek to invalidate WF!!!

Example: Reduction of thermodynamic Carnot efficiency, 1- T_C/T_H

For conversion of heat to electricity:

$$\gamma = \frac{\sqrt{(1+ZT)} - 1}{\sqrt{(1+ZT)} + \frac{T_C}{T_H}}.$$

Example: T_C/T_H =1/2, ZT = 3. Efficiency reduction **.4** .

Increasing S by a factor of two makes reduction ~ **.63**.

How to get large thermopowers

- Since an electron with energy E carries heat (see later)

E-μ:

Choosing $\mu = 0$:

$$S \equiv \frac{V}{\Delta T} = -\frac{L_{12}}{L_{11}} = \frac{\int dE\, E\sigma(E)\frac{\partial f}{\partial E}}{eT\int dE\,\sigma(E)\frac{\partial f}{\partial E}}.$$

Mott-Cutler
Phys Rev 181, 1336 (1969)

Sivan and Imry, 1986, from Landauer

Electrons and holes contribute opposite signs!

Want sharp, asymmetric $\sigma(E)$

II. Thermopower near the Anderson Transition

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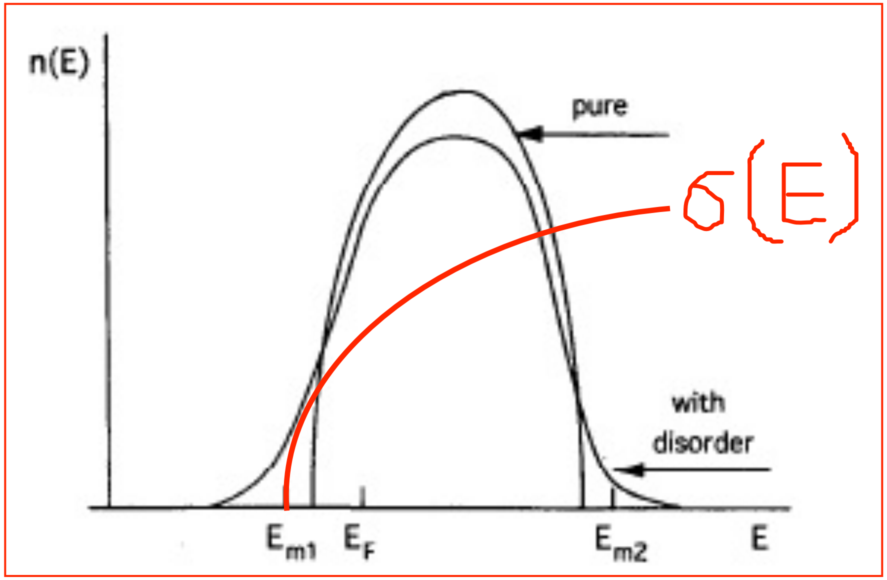
Need sharply changing σ(E)! and no e-h symmetry

- M-I transition: **$\sigma(E) \sim (E - E_m)^x$, near E_{m1}**



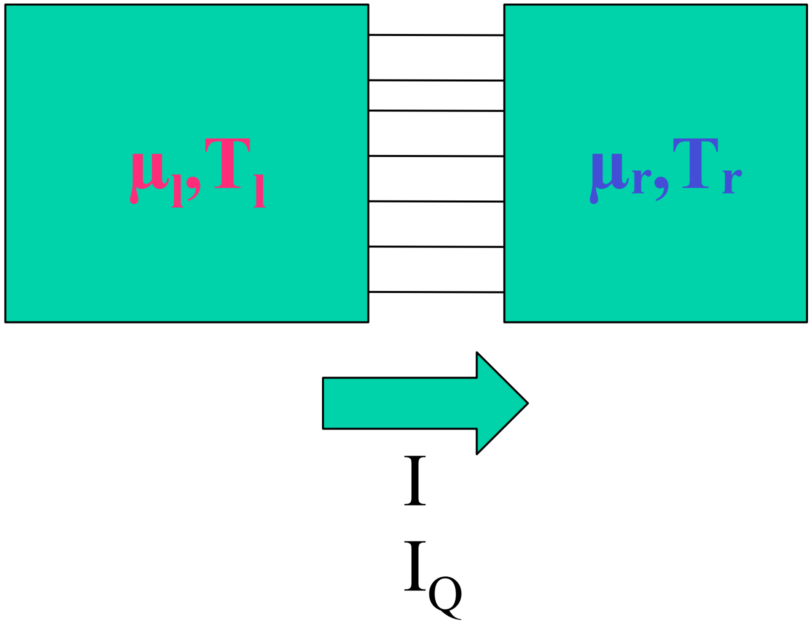
Basic theory: add thermal transport to the Thouless picture of conduction between two "blocks"

Thouless, D. J. (1977) Phys. Rev. Lett. 39, 1167.

$eV = \mu_l - \mu_r$

$\Delta T = T_l - T_r,$

Golden rule for interblock electron, Energy, heat transfer



Fundamental result: a particle leaving a system at energy E, carries heat (TdS) of E-μ

Entropy in that state is:

$$S_E = -k_B[f ln f + (1 \pm f) ln(1 \pm f)],$$

Bosons
Fermions

when the population, f, changes:

$$\dot{S}_E = -k_B \dot{f} ln \frac{f}{1 \pm f} = -\frac{E}{T}\dot{f},$$

(using equilibrium f, E measured from μ)

Two connected systems with voltage V and temp difference ΔT

$$\begin{pmatrix} I \\ I_Q \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} V \\ \Delta T \end{pmatrix},$$

I and I_Q conserved (no inelastic scattering).
But, due to V and ΔT get entropy production:

$$T\, dS/dT = IV + I_Q\, \Delta T/T$$

Rate of dissipation, generalizing Joule

Check: for photons/phonons, μ=0.

Thermal conductance "quantum", per mode in a (ballistic) waveguide is:

$$k_B^2 T\pi/(6\hbar) \ \text{(per mode)}$$

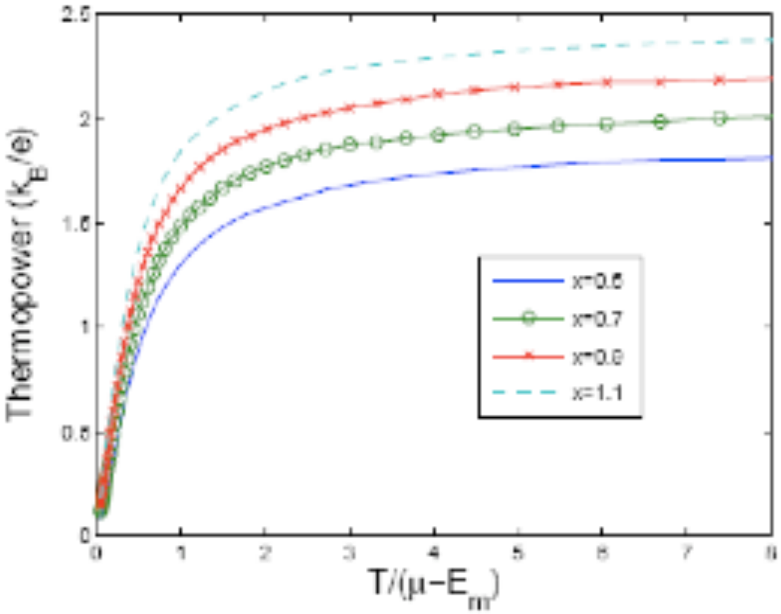
Kirczenow and Rego, 1998; cf YI derivation of e^2/h conductance quantum for electrons (1986).

- Derived full 2x2 “thermoelectric” matrix,
- Checked Onsager relations (incl magnetic field), (follow as identities)
- Wiedemann-Franz for (e’s) low-T thermal conductivity,
- Cutler-Mott for thermoelectric power.

Evaluating Mott-Cutler expression

near Anderson M-I transition (no serious interactions).

No inelastic scattering, no hopping cond.



$$S_{high} \approx \frac{1}{e}[2\log(2) + \mathrm{x}].$$

$$S_{low} \approx \frac{\pi^2 x T}{3e(\mu - E_m)} + O(T^3).$$

And S Scales (only deloc electrons):

$$S = Y(\frac{\mu - E_M}{T}),$$

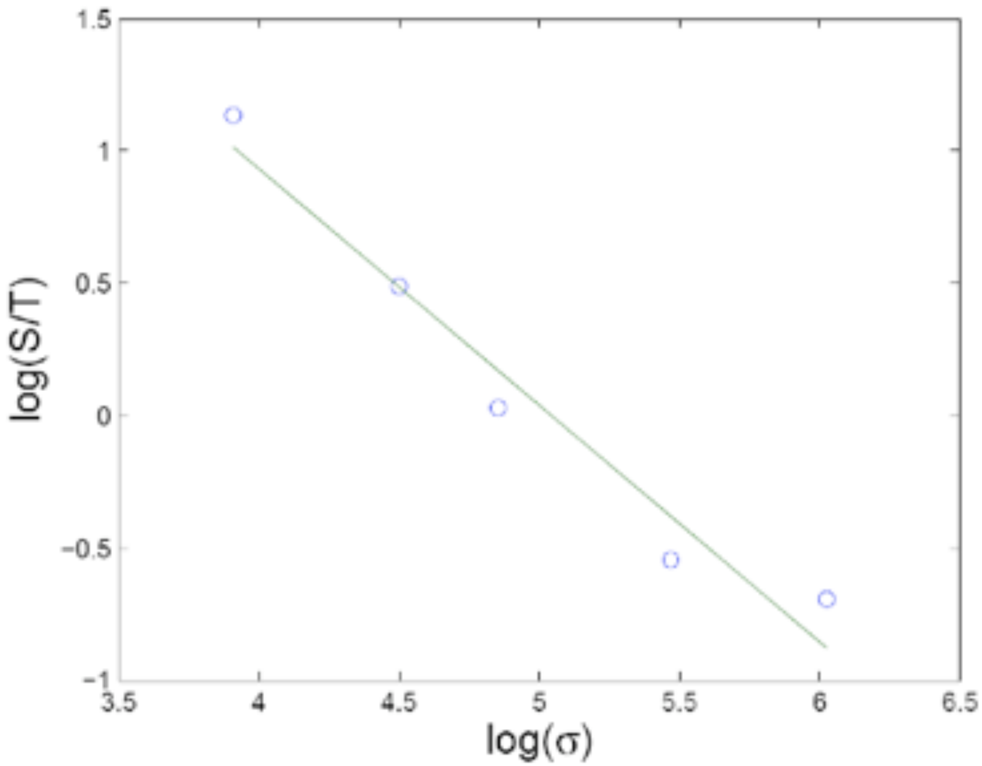
How to determine the critical exponent **x**?

- Usually, low temp σ_0 is plotted vs control parameter prop to μ-E_m (when both are small enough…)
- We suggest looking at low-temp slope of S,

and eliminating μ-E_m between it and σ (no need to know μ-E_m) :

$$\frac{dS}{dT}_{T\to 0} \sim [\sigma(T=0)]^{-1/x},$$

Applying this to existing data: Ovadyahu, J Phys C19, 5187 (1986), on InO_x



Get **x ~ 1-1.2**, need lower T, but good start!

See also; Lauinger and Baumann, J. Phys Cond Matt 7, 1305 (1995)

1312 *C Lauinger and F Baumann*

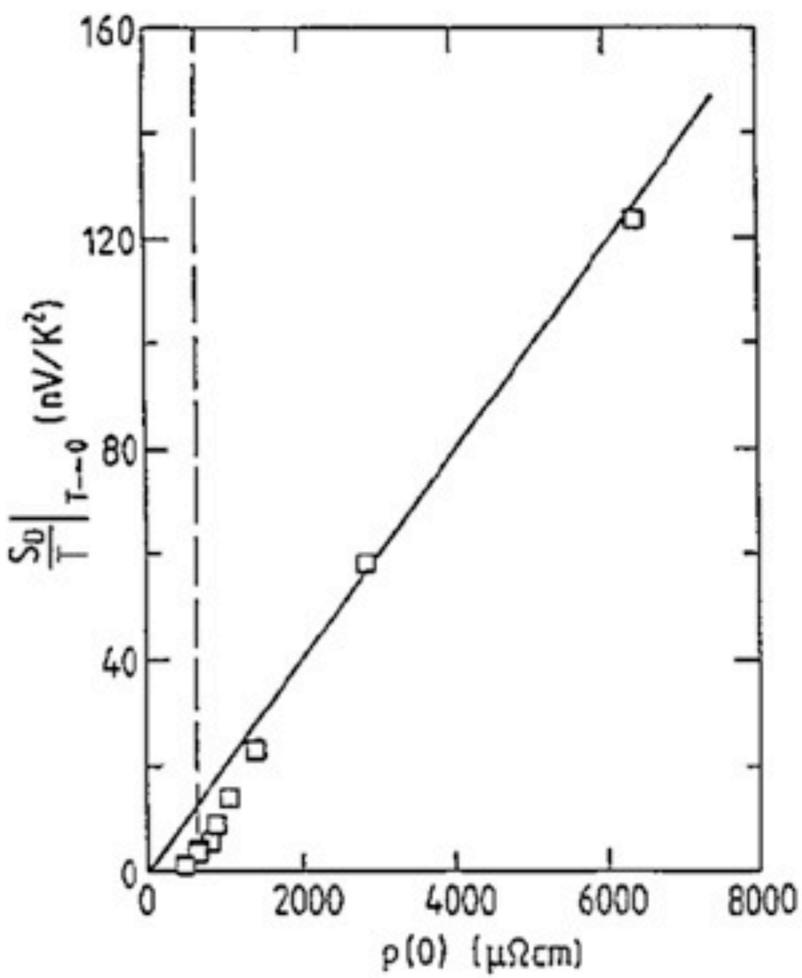


Figure 8. Low-temperature slope of S or S_D versus $\rho(0)$ for amorphous Au_xSb_{100-x}. For samples with $9 \leqslant x \leqslant 14.2$ at.% the values of $S(T)/T|_{T\to 0}$ are shown, while for samples with $x > 14.2$ at.% the values of $S_D(T)/T|_{T\to 0}$ taken from the fitting procedure are shown. All data were measured after annealing at 60 K. The solid line is a fit according to equation (5). The dashed line corresponds to the resistivity of a sample with $x = 14.2$ at.%.

Taken x = 1.

From exp papers:

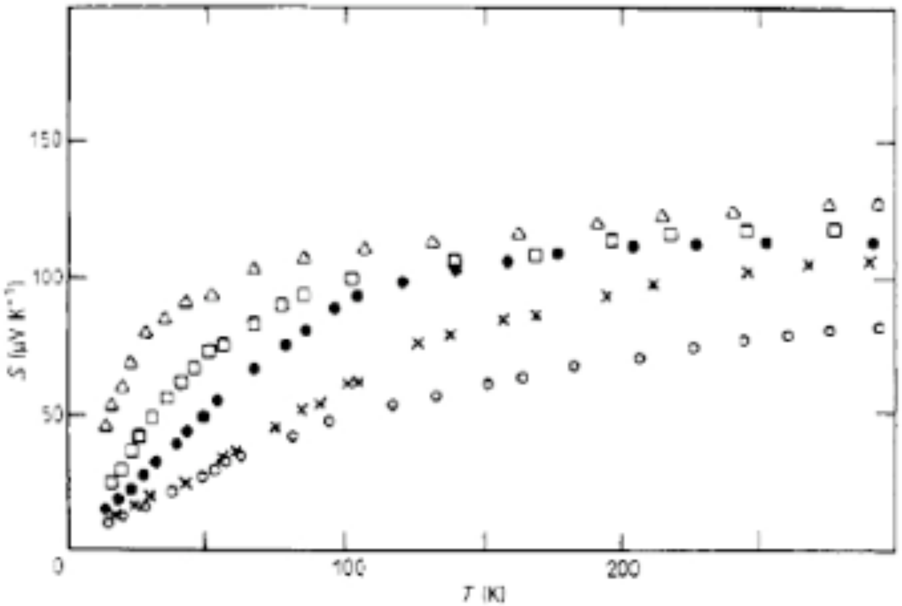


Figure 7. Thermoelectric power as a function of temperature for a batch of crystalline indium oxide samples (thickness ~1000 Å). The different curves were obtained by successively heat treating the as-prepared sample (designated by open circles) that had $\rho_{RT} = 1.7 \times 10^{-3}\ \Omega$ cm to obtain samples with $\rho_{RT} = 2.6 \times 10^{-3}$, 8.4×10^{-3}, 1.25×10^{-3}, $2 \times 10^{-3}\ \Omega$ cm (designated by crosses, full circles, squares and triangles respectively).

Ovadyahu, J Phys C (1986)

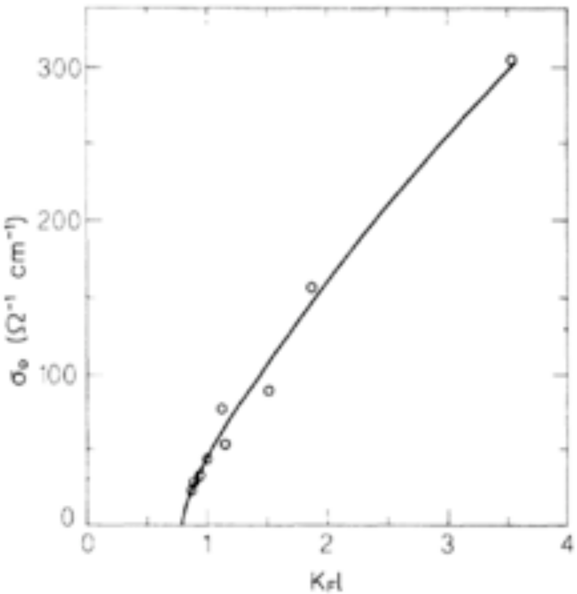
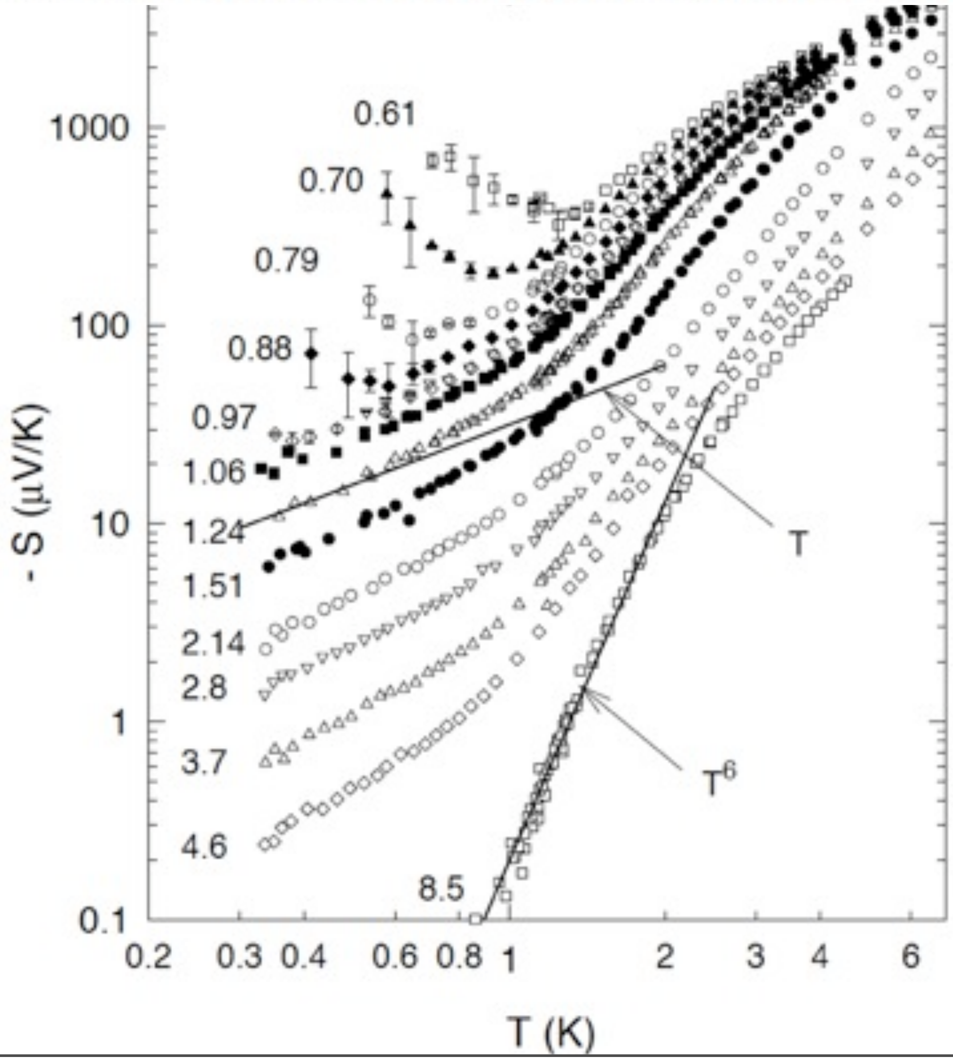


FIG. 2. The dependence of the extrapolated, zero-temperature conductivity, σ_0, on disorder. The solid line is given by $\sigma_0 = 141(K_F l - 0.80)^{0.75}$.

Ovadyahu and Tousson Phys. Rev. B **38**, 12290 (1988).

Critical behaviour of thermopower and conductivity at the metal-insulator transition in high-mobility Si-MOSFETs

R. Fletcher[a], V. M. Pudalov[b], A. D. B. Radcliffe[a] and C. Possanzini[c]



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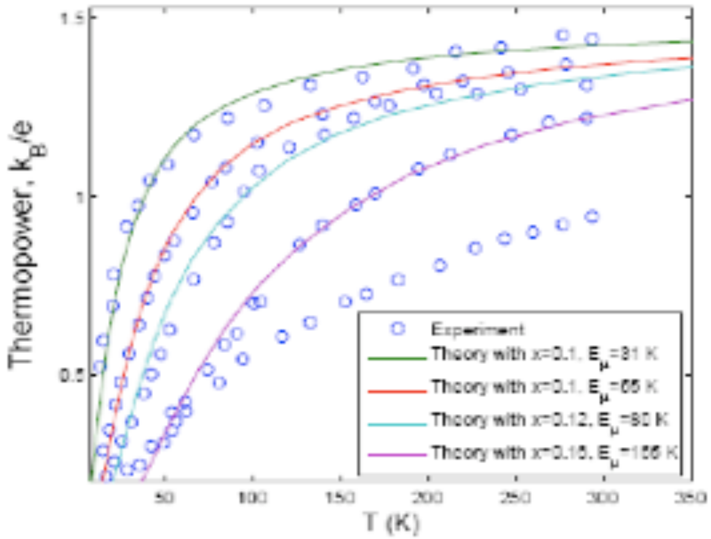
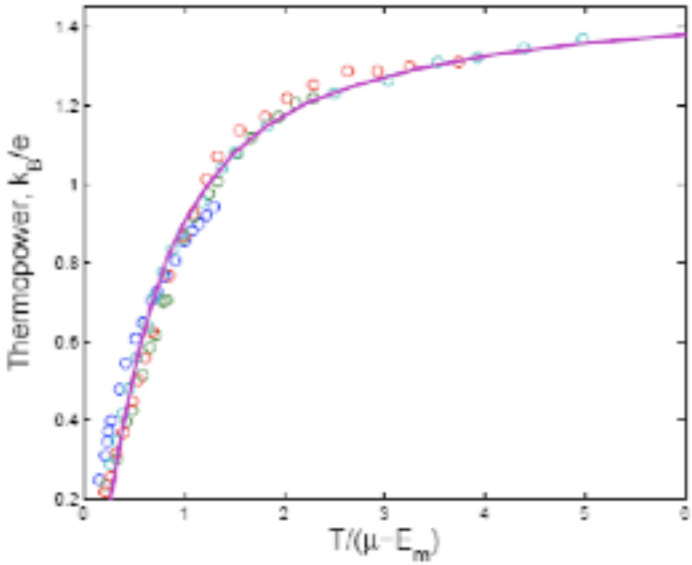
What about full scaling of S?

Nice, but takes us away from the QPT

and hopping is involved at the higher temps.





Good fit, but x ~.1 is unacceptable!

We believe that hopping below E_m reduces high T values.

Conclusion: Metal-Insulator Transition near "mobility edge":

$$\sigma_0(E) = A(E - E_m)^x$$

Offers a way to both:

1. Get large S, **and at low temps**.

2. Obtain valuable info on the critical behavior near the Anderson QPT.

Many more ideas to increase S!!!

III. Thermoelectric 3-terminal Transport in Molecular Junctions.

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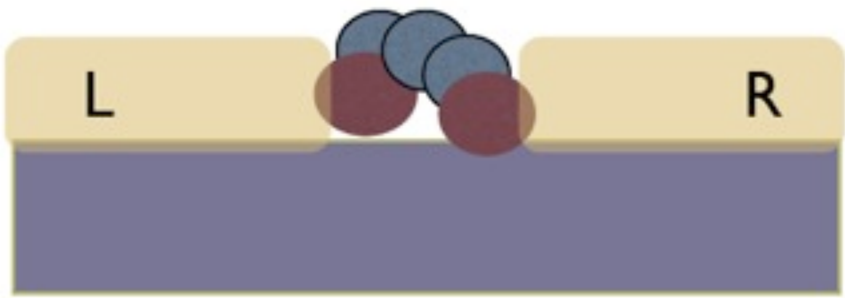
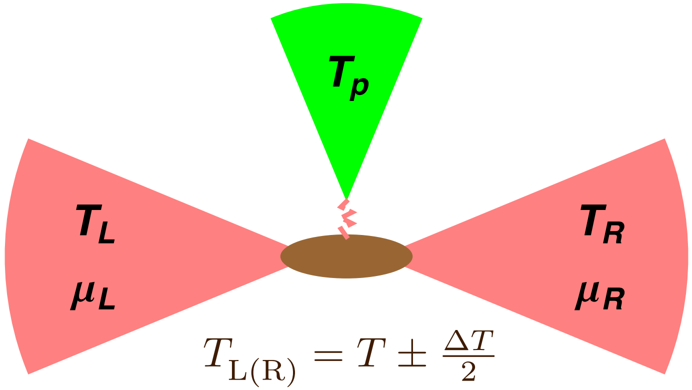
Molecular Junctions



- with Ora Entin-Wohlman, Amnon Aharony. PRB (2010)
- Including molecular vibrations and coupling to "substrate phonons"

thermoelectric transport through molecular bridges

$$TdS = dE - \mu dN$$



$$T_{\mathrm{L(R)}} = T \pm \frac{\Delta T}{2}$$
$$T_{\mathrm{P}} = T + \Delta T_{\mathrm{P}}$$
$$\mu_{\mathrm{L(R)}} = \mu \pm \frac{\Delta \mu}{2}$$

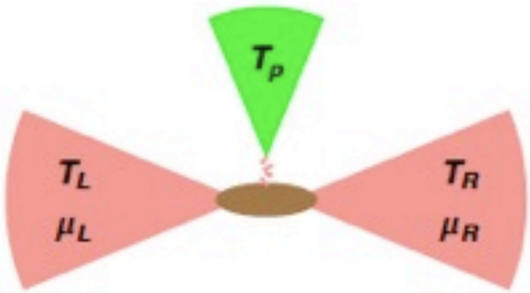
dissipation at reservoirs:

$$\dot{S}_{\mathrm{L(R)}} = \frac{1}{T_{\mathrm{L(R)}}}\left(\dot{E}_{\mathrm{L(R)}} - \mu_{\mathrm{L(R)}}\dot{N}_{\mathrm{L(R)}}\right)$$

entropy production of phonon bath:

$$\dot{S}_{\mathrm{P}} = \frac{1}{T_{\mathrm{P}}}\dot{E}_{\mathrm{P}}$$

Transport relations and entropy production



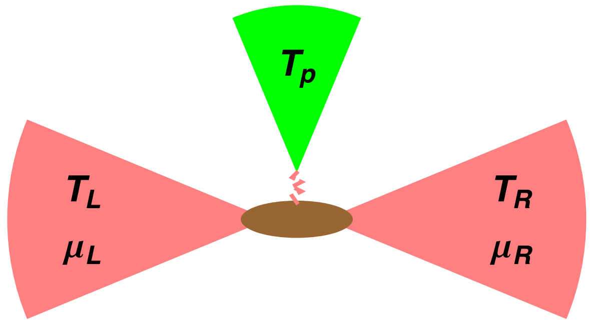
$$T_{\mathrm{L(R)}} = T \pm \tfrac{\Delta T}{2}$$
$$T_{\mathrm{P}} = T + \Delta T_{\mathrm{P}}$$
$$\mu_{\mathrm{L(R)}} = \mu \pm \tfrac{\Delta \mu}{2}$$

$$\dot{S}_{\mathrm{P}} + \dot{S}_{\mathrm{L}} + \dot{S}_{\mathrm{R}} = \frac{\Delta T_{\mathrm{P}}}{T^2} I_{\mathrm{QP}} + \frac{\Delta \mu / e}{T} I + \frac{\Delta T}{T^2} I_{\mathrm{Q}}$$

$$I = -\tfrac{e}{2}\left(\dot{N}_{\mathrm{L}} - \dot{N}_{\mathrm{R}}\right)$$
$$I_{\mathrm{Q}} = I_{\mathrm{E}} - \tfrac{\mu}{e} I \ , \quad I_{\mathrm{E}} = -\tfrac{1}{2}\left(\dot{E}_{\mathrm{L}} - \dot{E}_{\mathrm{R}}\right)$$
$$I_{\mathrm{QP}} = -\dot{E}_{\mathrm{P}} = \dot{E}_{\mathrm{L}} + \dot{E}_{\mathrm{R}}$$

linear-response thermoelectric transport

$$\begin{bmatrix} I \\ I_{\rm Q} \\ I_{\rm QP} \end{bmatrix} = \mathcal{M} \begin{bmatrix} \Delta\mu/e \\ \Delta T/T \\ \Delta T_{\rm P}/T \end{bmatrix}$$



$$\mathcal{M} = \begin{bmatrix} {\rm G} & {\rm K} & {\rm S}^{\rm P} \\ {\rm K} & {\rm K}_2 + {\rm K}_2^{\rm P} & \widetilde{\rm S}^{\rm P} \\ {\rm S}^{\rm P} & \widetilde{\rm S}^{\rm P} & {\rm C}^{\rm P} \end{bmatrix}$$

$$T_{\rm L(R)} = T \pm \frac{\Delta T}{2}$$
$$T_{\rm P} = T + \Delta T_{\rm P}$$
$$\mu_{\rm L(R)} = \mu \pm \frac{\Delta\mu}{2}$$

Onsager relations OK

$$\rm G = G^{el} + G^{inel} \ ,$$

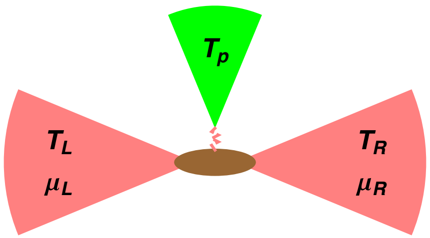
$$\mathrm{G^{el}} = \frac{e^2}{2\pi} \int d\omega F^{\rm el}(\omega)\Gamma_{\rm L}(\omega)\Gamma_{\rm R}(\omega),$$

$$\mathrm{G^{inel}} = \frac{e^2}{2\pi} \int d\omega F^{\rm inel}(\omega) \times \Big(\Gamma_{\rm L}(\omega_+)\Gamma_{\rm R}(\omega_-) + \Gamma_{\rm L}(\omega_-)\Gamma_{\rm R}(\omega_+)\Big) \ .$$

Thermoelectric transport coefficients (like 2-t)

$$\begin{bmatrix} I \\ I_{\rm Q} \\ I_{\rm QP} \end{bmatrix} = \mathcal{M} \begin{bmatrix} \Delta\mu/e \\ \Delta T/T \\ \Delta T_{\rm P}/T \end{bmatrix}$$

$$\mathcal{M} = \begin{bmatrix} {\rm G} & {\rm K} & {\rm S}^{\rm P} \\ {\rm K} & {\rm K}_2 + {\rm K}_2^{\rm P} & \widetilde{\rm S}^{\rm P} \\ {\rm S}^{\rm P} & \widetilde{\rm S}^{\rm P} & {\rm C}^{\rm P} \end{bmatrix}$$



$$T_{\rm L(R)} = T \pm \frac{\Delta T}{2}$$
$$T_{\rm P} = T + \Delta T_{\rm P}$$
$$\mu_{\rm L(R)} = \mu \pm \frac{\Delta\mu}{2}$$

$$\rm K = K^{el} + K^{inel} ,$$
$$\rm K_2 = K_2^{el} + K_2^{inel} ,$$

with

$$\mathrm{K}^{\rm el} = \frac{e}{2\pi}\int d\omega F^{\rm el}(\omega)(\omega-\mu)\Gamma_{\rm L}(\omega)\Gamma_{\rm R}(\omega),$$
$$\mathrm{K}^{\rm inel} = \frac{e}{2\pi}\int d\omega F^{\rm inel}(\omega)(\omega-\mu) \times \Big(\Gamma_{\rm L}(\omega_+)\Gamma_{\rm R}(\omega_-)+\Gamma_{\rm L}(\omega_-)\Gamma_{\rm R}(\omega_+)\Big) ,$$

and

$$\mathrm{K}_2^{\rm el} = \frac{1}{2\pi}\int d\omega F^{\rm el}(\omega)(\omega-\mu)^2\Gamma_{\rm L}(\omega)\Gamma_{\rm R}(\omega),$$
$$\mathrm{K}_2^{\rm inel} = \frac{1}{2\pi}\int d\omega F^{\rm inel}(\omega)(\omega-\mu)^2 \times \Big(\Gamma_{\rm L}(\omega_+)\Gamma_{\rm R}(\omega_-)+\Gamma_{\rm L}(\omega_-)\Gamma_{\rm R}(\omega_+)\Big) .$$

$$F^{\rm el}(\omega) = \beta|G(\omega)|^2 f(\omega)[1-f(\omega)]$$

$$F^{\rm inel}(\omega) = \beta\frac{\gamma^2}{e^{\beta\omega_0}-1}|G(\omega_+)|^2|G(\omega_-)|^2 f(\omega_-)[1-f(\omega_+)]$$

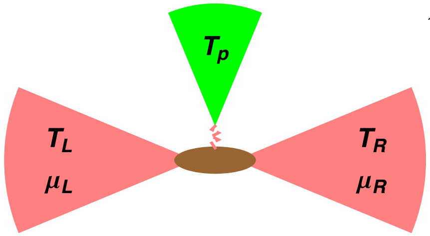
$$\omega_\pm = \omega \pm \frac{\omega_0}{2}$$

thermoelectric transport coefficients (novel - 3t)

$$\begin{bmatrix} I \\ I_{\rm Q} \\ I_{\rm QP} \end{bmatrix} = \mathcal{M} \begin{bmatrix} \Delta\mu/e \\ \Delta T/T \\ \Delta T_{\rm P}/T \end{bmatrix}$$

$$\mathcal{M} = \begin{bmatrix} {\rm G} & {\rm K} & {\rm S^P} \\ {\rm K} & {\rm K_2 + K_2^P} & \widetilde{\rm S}^{\rm P} \\ {\rm S^P} & \widetilde{\rm S}^{\rm P} & {\rm C^P} \end{bmatrix}$$

$$\mathrm{S^P} = \frac{e\omega_0}{2\pi}\int d\omega F^{\rm inel}(\omega) \times \Big(\Gamma_{\rm R}(\omega_+)\Gamma_{\rm L}(\omega_-) - \Gamma_{\rm L}(\omega_+)\Gamma_{\rm R}(\omega_-)\Big)$$



$$\widetilde{\rm S}^{\rm P} = \frac{\omega_0}{2\pi}\int d\omega F^{\rm inel}(\omega)\Big[(\omega-\mu)\Big(\Gamma_{\rm R}(\omega_+)\Gamma_{\rm L}(\omega_-) - \Gamma_{\rm L}(\omega_+)\Gamma_{\rm R}(\omega_-)\Big) + \frac{\omega_0}{2}\Big(\Gamma_{\rm R}(\omega_+)\Gamma_{\rm R}(\omega_-) - \Gamma_{\rm L}(\omega_+)\Gamma_{\rm L}(\omega_-)\Big)\Big],$$

$$T_{\rm L(R)} = T \pm \frac{\Delta T}{2}$$

$$T_{\rm P} = T + \Delta T_{\rm P}$$

$$\mu_{\rm L(R)} = \mu \pm \frac{\Delta\mu}{2}$$

IV, Hopping 3t Thermoelectrity

- Two-site case
- Longer chains, dominance of edges

role of inelastic interactions

to force electrons transported through a junction, e.g., one-dimensional nanosystems, to take relatively large and well-defined energy from the phonons and deliver it to another bath or to an electronic reservoir, as a heat or as a (charge) current.

Generalization of Mahan-Sofo!

three-terminal realization of Mahan-Sofo

new element: inelastic processes

$$\sigma = \int dE \sigma(E)[-\partial f(E)/\partial E]$$

$$\mathrm{T}\sigma S = \frac{1}{e}\int dE E \sigma(E)[-\partial f(E)/\partial E]$$

$$\mathrm{T}\kappa_2 = \frac{1}{e^2}\int dE E^2 \sigma(E)[-\partial f(E)/\partial E]$$

$$\kappa_{\mathrm{e}} = \kappa_2 - \sigma S^2 \mathrm{T}$$

$$\kappa_{\mathrm{e}} \to \langle E^2 \rangle - \langle E \rangle^2$$

$$ZT = \mathrm{T}\sigma S^2/(\kappa_{\mathrm{e}} + \kappa_{\mathrm{ph}}) \to \mathrm{T}\sigma S^2/\kappa_{\mathrm{ph}}$$

limited by thermal conductivity of the phonons, Wiedmann-Franz law not in action; fails totally, Ke=0, with very narrow transport energy-band

related ideas:

Kharpai,Ludwig,Kotthous,Tranitz,Wegscheider, Phys. Rev. Lett. **97**, 176803 (2006): Ratchet converting phonon-induced excitations into dc current in QPC's

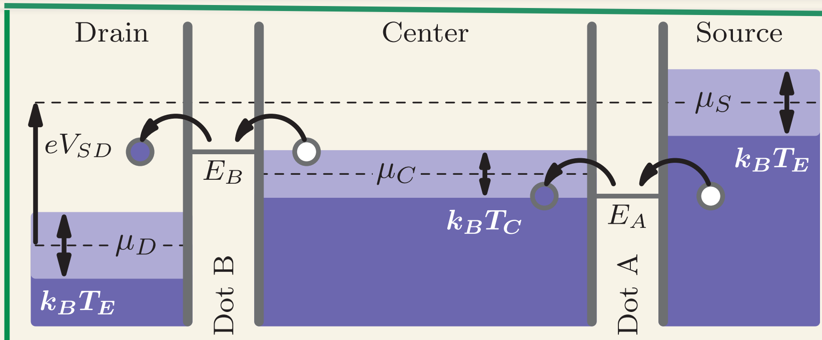


FIG. 1 (color online). QDR energies in the cooling regime. Thermal broadening in the three 2DEGs (source, center and drain) is shown by the light shading around their electrochemical potentials (μ_S, μ_C, μ_D). The net flow of an electron from source to drain removes an energy $E_B - E_A$ from the center. E_A (E_B) is the ground state addition energy of dot A (B).

Prance,Smith,Griffiths,Chorley,Anderson,Jones,Farrer,Ritchie, Phys. Rev. Lett. **102**, 146602 (2009): Cooling 2DEG using Qdots, cool e's in hot e's out

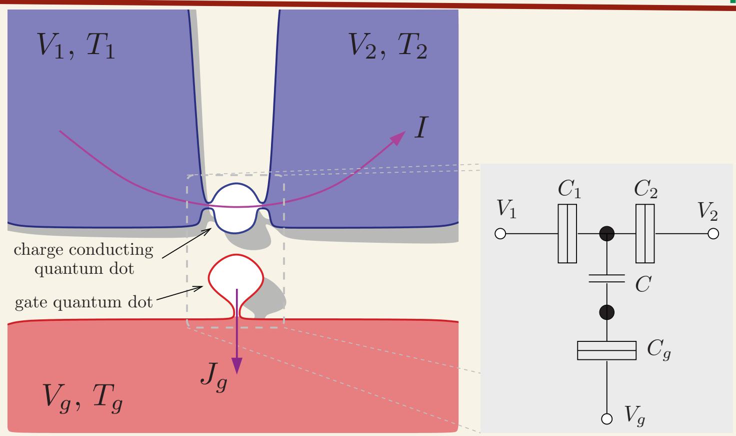
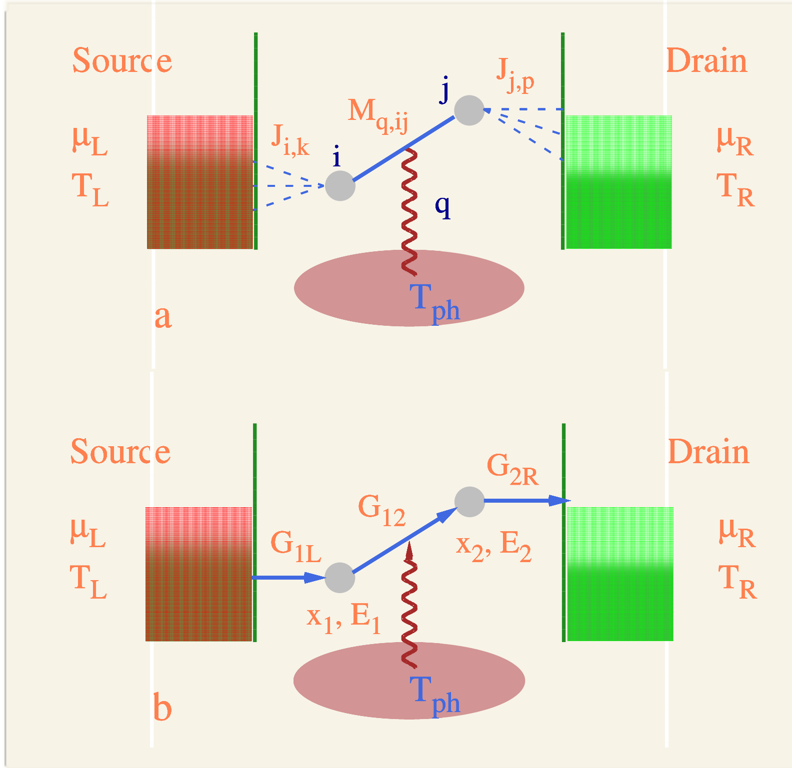


FIG. 1. (Color online) Energy to current converter. The conductor, a quantum dot open to transport between two fermionic reservoirs at voltages V_1 and V_2 and temperatures T_1 and T_2, is coupled capacitively to a second dot which acts as a fluctuating gate coupled to a reservoir at voltage V_g and temperature T_g. Here we discuss the case $T_1 = T_2 = T_s$.

Sanchez and Buttiker, Phys. Rev. B **83**, 085428 (2011):Optimal conversion of heat into electric flow by coupling to quantized levels tunneling conductance:

$$G_{\rm tun} \simeq e^2 \frac{1}{E_i^2 E_j^2} \nu_L \nu_R |\alpha_e|^6 e^{-2W/\xi}$$



hopping conductance:

$$G_{ij} \simeq e^2 |\alpha_{\rm e-ph}|^2 \nu_{\rm ph}(|E_{ij}|) \times \frac{1}{k_{\rm B}{\rm T}} e^{-2|x_{ij}|/\xi} e^{-(|E|_i + |E_j| + |E_{ij}|)/(2k_{\rm B}{\rm T})}$$

golden-rule transition rate (inelastic transitions):

$$\Gamma_{ij} = 2\pi\Gamma_{\mathrm{in}} f_i(1 - f_j)\mathrm{N_B}(E_{ji})$$

distributions:

$$f_i = \frac{1}{\exp\left(\frac{E_i - \mu_i}{k_\mathrm{B}\mathrm{T}_i}\right) + 1}$$

$$\mathrm{N_B} = \frac{1}{\exp\left(\frac{\omega_q}{k_\mathrm{B}\mathrm{T}_\mathrm{ph}}\right) + 1}$$

the two-site case

currents:

$$I = e(\Gamma_{12} - \Gamma_{21})$$

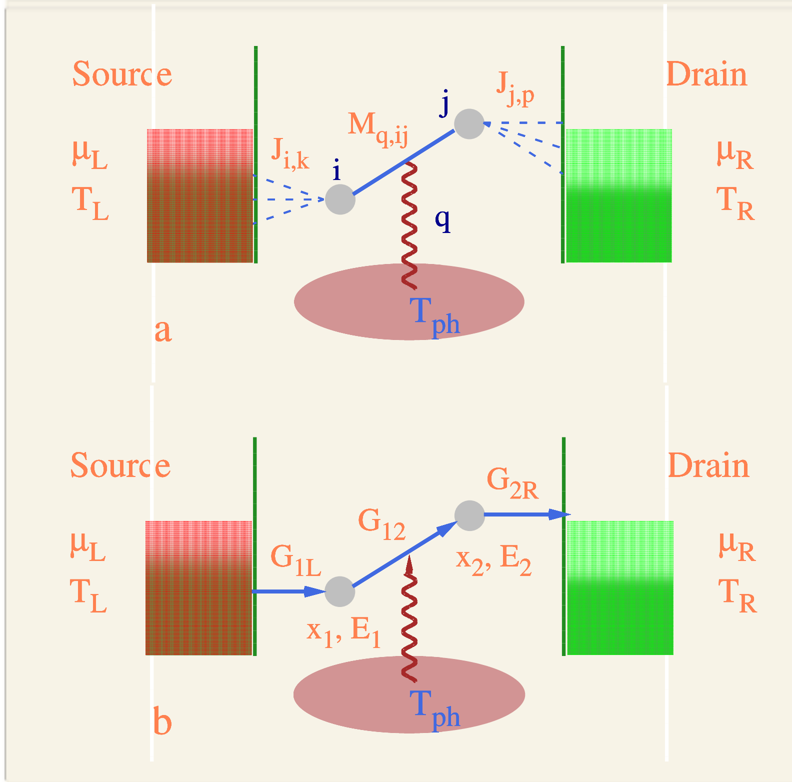
$$I_Q^\mathrm{e} = \overline{E}(\Gamma_{12} - \Gamma_{21})$$

$$I_Q^\mathrm{ph} = E_{21}(\Gamma_{12} - \Gamma_{21})$$

$$\overline{E} = (E_1 + E_2)/2$$

$$E_{21} = E_2 - E_1$$

"ordinary" figure of merit:
limited by phonon heat conductivity



"new" figure of merit for the efficiency

$$\eta = I_Q^{\rm ph}/(eIV)$$

$$\widetilde{Z}\mathrm{T} \rightarrow \infty$$

Onsager matrix:

$$\begin{bmatrix} I \\ I_Q^{\rm e} \\ I_Q^{\rm ph} \end{bmatrix} = G \begin{bmatrix} 1 & \overline{E}/e & E_{21}/e \\ \overline{E}/e & \overline{E}^2/e^2 & \overline{E}E_{21}/e^2 \\ E_{21}/e & \overline{E}E_{21}/e^2 & E_{21}^2/e^2 \end{bmatrix} \begin{bmatrix} V \\ \Delta\mathrm{T}/\mathrm{T} \\ \Delta\mathrm{T}_{\rm ph}/\mathrm{T} \end{bmatrix}$$

"new" figure of merit for the efficiency--more realistic case

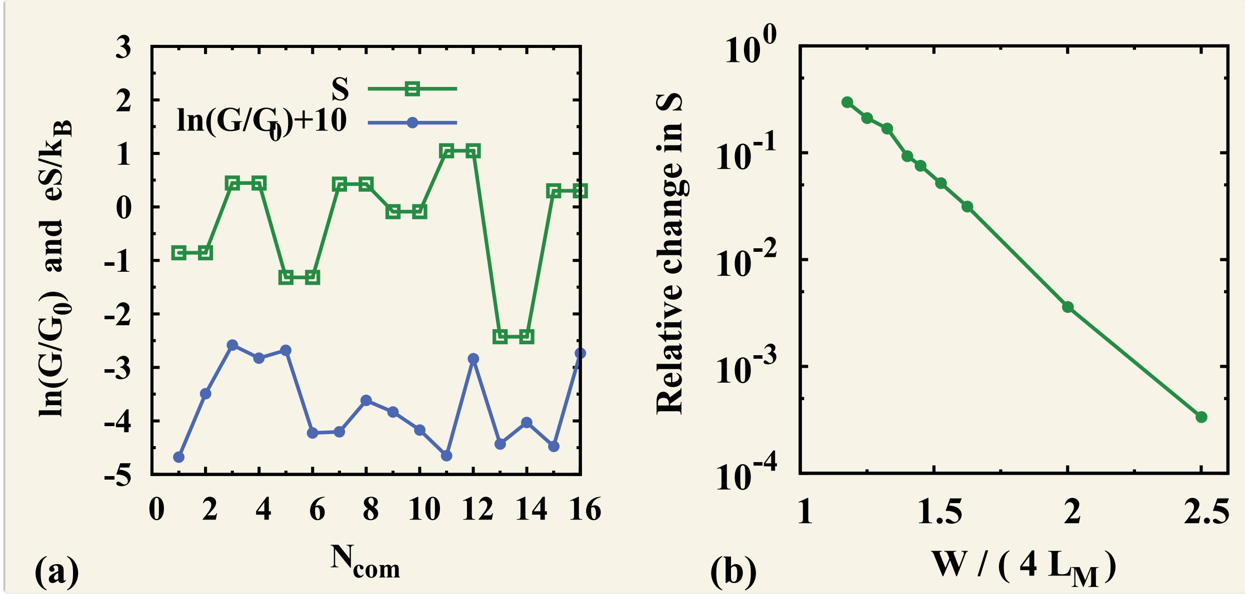
$$\eta = I_Q^{\mathrm{ph}}/(eIV)$$

wasted work due to parasitic heat diffusion from the leads to the system being cooled, and elastic tunneling conductance

$$\widetilde{Z}\mathrm{T} = \Big[\frac{G_{\mathrm{el}}}{G} + \frac{K_{\mathrm{pp}}}{K_{\mathrm{pe}}} + \frac{G_{\mathrm{el}} K_{\mathrm{pp}}}{G K_{\mathrm{pe}}}\Big]^{-1}$$

$$K_{pe} = \frac{G}{e^2} E_{21}^2$$

the one-dimensional chain -- only edges matter



the conductance is sensitive to changes in the configuration within the sample, the thermopower is not!

Ongoing and future Work

Effect of breaking of time-reversal symmetry

S below mobilty edge and in Anderson Insulator

$S_{xy}(B)$ (Nernst-Ettinghausen)

Phonon (and other bosons) drag

Effect of electron correlations.

THANK YOU!!!