Reaching optimal efficiencies using nano-sized photo-electric devices

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in collab. with Bob Rutten and Massimiliano Esposito

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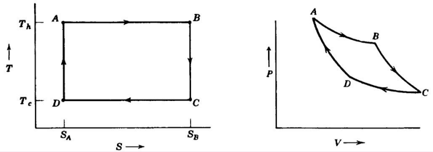
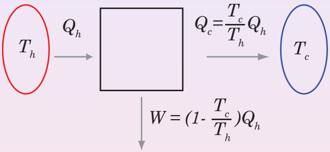
Introduction: Carnot efficiency

$$\eta_c = 1 - \frac{T_c}{T_h}$$

Sadi Carnot
(1796-1832)





- fundamental result, universal upper limit
- no energy losses
- reversible operation (entropy production = 0)
  - $\longrightarrow$ isothermal parts are infinitely slowly
  - $\longrightarrow$ $\text{power} = 0 = \frac{\text{work}}{\text{cycle time} \rightarrow \infty}$

solar cells:

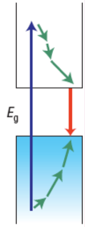
$$\eta_c \approx 95\%$$

in reality: lower efficiency

$$\eta \approx 24\%$$

reasons:

- energy losses / dissipation
  - heat generation due to electron/hole relaxation within band
  - thermal recombination processes
- non-zero power output / irreversible operation
  in practice: operation at maximum power output



Introduction: efficiency at maximum power

F.L. Curzon and B. Ahlborn, *Am. J. Phys.* 43, 1974

Efficiency of a Carnot Engine at Maximum Power Output

$$\eta_{ca} = 1 - \sqrt{\frac{T_c}{T_h}}$$

remarks: (cfr. previous talk)

- not an upper limit ↔ Carnot (see further)
- eff. @ max. power: highest for strongly coupled systems
- universality for strongly coupled systems in the linear term:

$$\eta = \frac{\eta_c}{2} + O(\eta_c^2)$$

and sometimes also in the quadratic term

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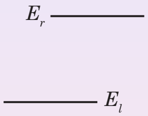
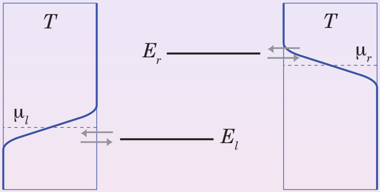
topic of this talk:
efficiency at maximum power of a *nano-sized solar cell*

Nano solar cell



- nano structure with 2 energy levels (no band structure!)

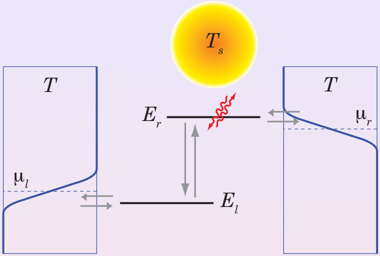
Nano solar cell



- nano structure with 2 energy levels (no band structure!)
- contacts: two electron reservoirs at the same (ambient) temperature but with different chemical potential

$$\mu_r = \mu_l + qV$$

Nano solar cell



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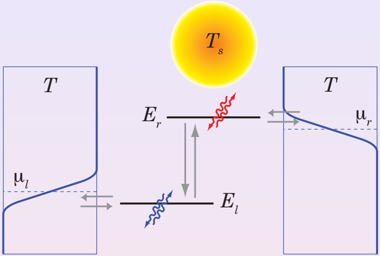
- solar excitation/recombination of electrons

Nano solar cell

"a minimal model for solar energy conversion"



- nano structure with 2 energy levels (no band structure!)
- contacts: two electron reservoirs at the same (ambient) temperature but with different chemical potential

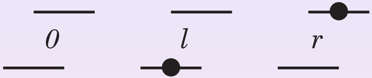
$$\mu_r = \mu_l + qV$$

- solar excitation/recombination of electrons
- thermal (non-radiative) excitation/recombination of electrons

Nano solar cell: electron dynamics

flow of electrons: stochastic description

(master equation for driven open quantum systems)



$$\begin{bmatrix} \dot{p}_0(t) \\ \dot{p}_l(t) \\ \dot{p}_r(t) \end{bmatrix} = \begin{bmatrix} -k_{l0}-k_{r0} & k_{0l} & k_{0r} \\ k_{l0} & -k_{0l}-k_{lr} & k_{rl} \\ k_{r0} & k_{rl} & -k_{0r}-k_{lr} \end{bmatrix} \begin{bmatrix} p_0(t) \\ p_l(t) \\ p_r(t) \end{bmatrix}$$

$$k_{l0} = \Gamma_l f(x_l) \quad ; \quad k_{0l} = \Gamma_l [1 - f(x_l)]$$

$$k_{r0} = \Gamma_r f(x_r) \quad ; \quad k_{0r} = \Gamma_r [1 - f(x_r)]$$

$$k_{rl} = \Gamma_{nr} n(x_g) + \Gamma_s n(x_s)$$

$$k_{lr} = \Gamma_{nr}[1 + n(x_g)] + \Gamma_s [1 + n(x_s)]$$

$$f(x) = [\exp(x) + 1]^{-1}$$

$$n(x) = [\exp(x) - 1]^{-1}$$

$$x_l = \frac{E_l - \mu_l}{T} \quad ; \quad x_r = \frac{E_r - \mu_r}{T} \quad ; \quad x_g = \frac{E_r - E_l}{T} \quad ; \quad x_s = \frac{E_r - E_l}{T_s}$$

coupling constants with the reservoirs: Γ_l, Γ_r, Γ_{nr} and Γ_s

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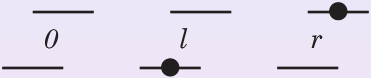

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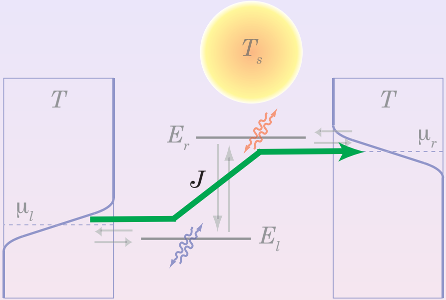
in equilibrium: grand-canonical distribution $p_i \propto e^{-\beta(E_i - \mu)}$

Nano solar cell: electron dynamics

stationary electron (particle) current: $J = k_{l0}p_0 - k_{0l}p_l$



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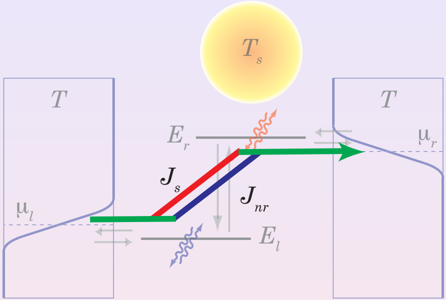


two contributions:

$$J = J_s + J_{nr}$$

with:

$$J_s \quad \rightarrow \quad \text{pumping of sun}, \ \propto \Gamma_s$$
$$J_{nr} \quad \rightarrow \quad \text{non-radiative excitation/recombination}, \ \propto \Gamma_{nr}$$

Nano solar cell: thermodynamics

- heat flows due to excitation/recombination:

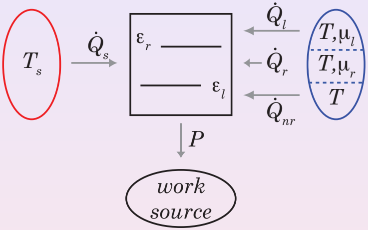
$$\dot{Q}_s = (E_r - E_l)J_s$$
$$\dot{Q}_{nr} = (E_r - E_l)J_{nr}$$

- heat flows from contacts:

$$\dot{Q}_l = (E_l - \mu_l)J$$
$$\dot{Q}_r = (E_r - \mu_r)J$$

- power: conservation of energy

$$P = (\mu_r - \mu_l)J = (qJ)V$$



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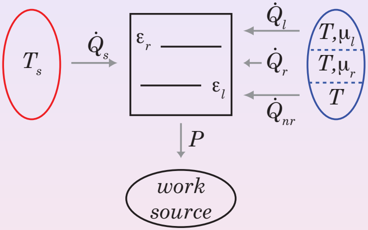
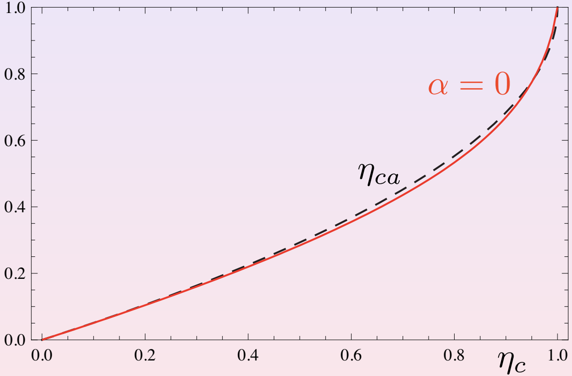


efficiency:

$$\eta = \frac{P}{\dot{Q}_s} = \frac{(\mu_r - \mu_l)J}{(E_r - E_l)J_s}$$

Nano solar cell: efficiency at maximum power

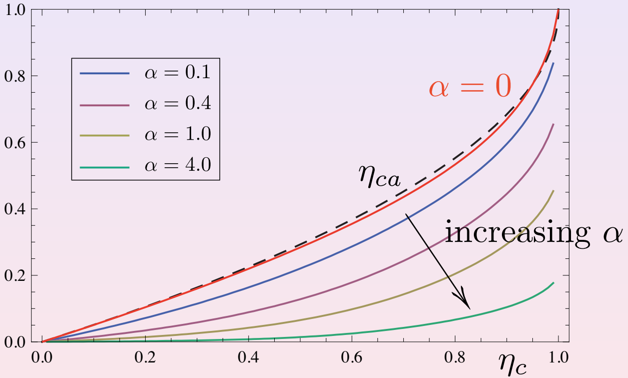
setting $\Gamma_{nr} = 0$ only solar excitation/recombination $J = J_s$
each absorbed photon pumps one electron !



[$\Gamma_l = \Gamma_r = \Gamma_s = \Gamma$ and $\Gamma_{nr} = \alpha\Gamma$]

Nano solar cell: efficiency at maximum power

setting $\Gamma_{nr} = 0$ only solar excitation/recombination $J = J_s$
when $\Gamma_{nr} \neq 0$ $\longrightarrow$ decrease of efficiency due to dissipation



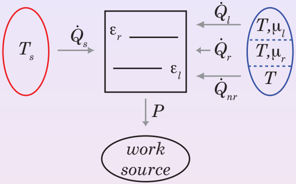
[$\Gamma_l = \Gamma_r = \Gamma_s = \Gamma$ and $\Gamma_{nr} = \alpha\Gamma$]

Nano solar cell: efficiency at maximum power

entropy production:

$$\dot{S}_i = -\frac{\dot{Q}_s}{T_s} - \frac{\dot{Q}_l + \dot{Q}_r + \dot{Q}_{nr}}{T}$$

Since $P = \dot{Q}_s + \dot{Q}_l + \dot{Q}_r + \dot{Q}_{nr}$



combination gives the familiar expression:

$$\dot{S}_i = \dot{Q}_s F_U + J F_N$$

with thermodynamic forces:

$$F_U = \frac{1}{T} - \frac{1}{T_s} \quad ; \quad F_N = \frac{\mu_l - \mu_r}{T} \quad \left(= -\frac{qV}{T} \right)$$

Nano solar cell: efficiency at maximum power

linear regime (small thermodynamic forces):

- $\dot{Q}_s \approx L_{UU}F_U + L_{UN}F_N$
- $J \approx L_{NU}F_U + L_{NN}F_N$

- L_{ij} = Onsager coefficients
- $L_{NU} = L_{UN}$: cross coupling

@ max. power:

$$\eta = \frac{\eta_c}{2}\frac{\kappa^2}{2-\kappa^2} \qquad \dot{S}_i = F_U^2 L_{UU}\left(1-\frac{3}{4}\kappa^2\right)$$

with:

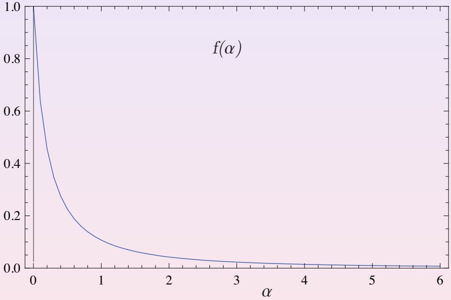
$$\kappa^2 = \frac{e^{x_l}(e^{x_g}-1)\Gamma_l\Gamma_r\Gamma_s}{\left[\Gamma_{nr}(\Gamma_l+\Gamma_r)+e^{x_l}\left((\Gamma_{nr}-\Gamma_l)\Gamma_r + e^{x_g}\Gamma_l(\Gamma_{nr}+\Gamma_r)\right)\right](\Gamma_{nr}+\Gamma_s)}$$

efficiency is maximal when $\kappa^2 = 1 \rightarrow$ **STRONG COUPLING** and determinant of Onsager matrix = 0

Nano solar cell: efficiency at maximum power

setting $\Gamma_l = \Gamma_r = \Gamma_s = \Gamma$ and $\Gamma_{nr} = \alpha\Gamma$ gives:

$$\eta = \frac{\eta_c}{2} f(\alpha)$$



→ without strong coupling: fast decrease of efficiency

Nano solar cell: efficiency at maximum power

Second order expansion (still strong coupling):

$$\eta = \frac{\eta_c}{2} + 0.09288\eta_c^2 + \dots$$

No universality!

Nano solar cell: efficiency at maximum power

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$$\eta = \frac{\eta_c}{2} + 0.09288\eta_c^2 + \dots \qquad \text{No universality!}$$

No collapse of forces and fluxes at second order!

$$J = L\mathcal{F} + (M_{UU}F_U^2 + M_{UN}F_UF_N + M_{NN}F_N^2) + \dots$$

with $\mathcal{F} = (E_r - E_l)F_U + F_N$

Nano solar cell: efficiency at maximum power

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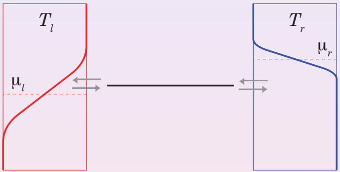
But:

$$M_{UU} - E_gM_{UN} + E_g^2M_{NN} = 0$$

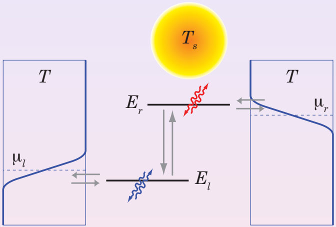
as a consequence of the fluctuation theorem

Nano solar cell: efficiency at maximum power

Thermoelectric converter:



Solar energy converter:



Nano solar cell: efficiency at maximum power

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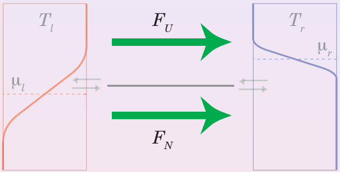
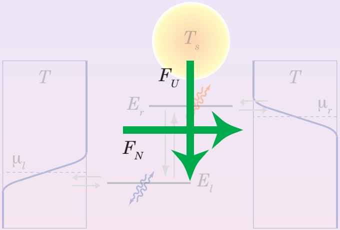


2 reservoirs
Fermi statistics

Solar energy converter:



3 reservoirs
mixed statistics (Fermi - Bose)

Conclusion

- microscopic/thermodynamic description of energy conversion in nano-sized solar cells
- in the ideal limit: solar cell is strongly coupled;
  efficiency close to Curzon-Ahlborn
- for weak coupling: fast decrease of efficiency
- universality only in the linear regime
- no collapse of second-order coefficients
  $\leftrightarrow$ thermoelectric *vs.* solar energy converters.

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Thank You !