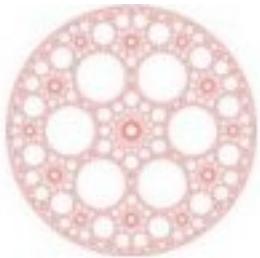


# Introduction to a few basic concepts in thermoelectricity

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# Irreversible thermodynamic

Irreversible thermodynamics based on the postulates of equilibrium electrostatics plus the postulate of **time-reversal symmetry of physical laws** (if time  $t$  is replaced by  $-t$  and simultaneously applied magnetic field  $\mathbf{B}$  by  $-\mathbf{B}$ )

The thermodynamic theory of irreversible processes is based on the **Onsager Reciprocity Theorem**

# Thermodynamic forces and fluxes

Irreversible processes are driven by **thermodynamic forces** (or generalized forces or affinities)  $X_i$

**Fluxes**  $J_i$  characterize the response of the system to the applied forces

**Entropy production rate** given by the sum of the products of each flux with its associated thermodynamic force

$$S = S(U, V, N_1, N_2, \dots) = S(E_0, E_1, E_2, \dots)$$

$$\frac{dS}{dt} = \sum_k \frac{\partial S}{\partial E_k} \frac{dE_k}{dt} = \sum_k X_k J_k$$

# Linear response

Purely resistive systems: fluxes at a given instant depend only on the thermodynamic forces at that instant (memory effects not considered)

$$J_i = \sum_j L_{ij} X_j + \frac{1}{2} \sum_{jk} L_{ijk} X_j X_k + \dots$$

Fluxes vanish as thermodynamic forces vanish

Linear (and purely resistive) processes:

$$J_i = \sum_j L_{ij} X_j$$

$L_{ij}$  Onsager coefficients (first-order kinetic coefficients) depend on intensive quantities (T,P, $\mu$ ,...)

Phenomenological linear Ohm's, Fourier's, Fick's laws

# Onsager-Casimir reciprocal relations

$$L_{ij}(\mathbf{B}) = L_{ji}(-\mathbf{B})$$

Relationship of Onsager theorem to time-reversal symmetry of physical laws

Consider **delayed correlation moments of fluctuations** (for simplicity without applied magnetic fields)

$$\delta E_j(t) \equiv E_j(t) - E_j, \quad \langle \delta E_j \rangle = 0,$$

$$\langle \delta E_j(t) \delta E_k(t + \tau) \rangle = \langle \delta E_j(t) \delta E_k(t - \tau) \rangle = \langle \delta E_j(t + \tau) \delta E_k(t) \rangle$$

$$\lim_{\tau \rightarrow 0} \left\langle \delta E_j(t) \frac{\delta E_k(t + \tau) - \delta E_k(t)}{\tau} \right\rangle = \lim_{\tau \rightarrow 0} \left\langle \frac{\delta E_j(t + \tau) - \delta E_j(t)}{\tau} \delta E_k(t) \right\rangle$$

$$\langle \delta E_j \delta \dot{E}_k \rangle = \langle \delta \dot{E}_j \delta E_k \rangle$$

Assume that fluctuations decay is governed by the same linear dynamical laws as are macroscopic processes

$$\delta \dot{E}_k = \sum_l L_{kl} \delta X_l$$

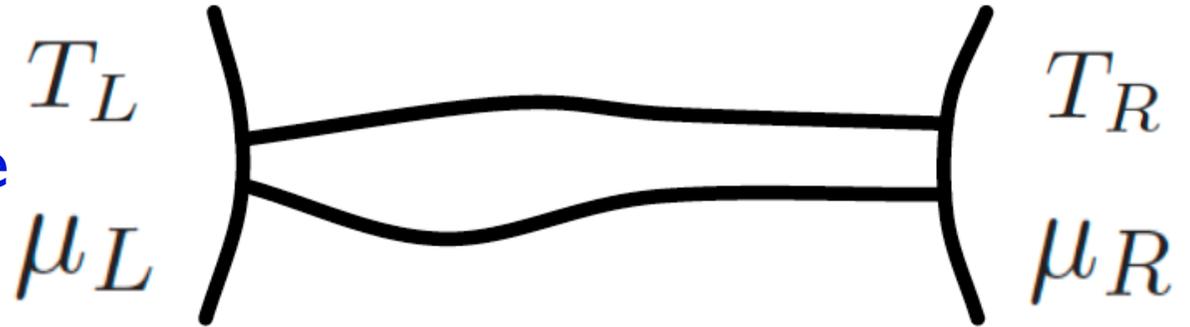
$$\sum_l L_{kl} \langle \delta E_j \delta X_l \rangle = \sum_l L_{jl} \langle \delta X_l \delta E_k \rangle$$

Assume that the fluctuation of each thermodynamic force is associated only with the fluctuation of the corresponding extensive variable

$$\langle \delta E_j \delta X_l \rangle = 0 \text{ if } l \neq j$$

# Steady state heat to work conversion

**Stochastic baths:** ideal gases at fixed temperature and chemical potential



$$\begin{cases} J_\rho = L_{\rho\rho}X_1 + L_{\rho q}X_2 \\ J_q = L_{q\rho}X_1 + L_{qq}X_2 \end{cases}$$

$$X_1 = -\beta\Delta\mu$$

$$X_2 = \Delta\beta \approx -\Delta T/T^2$$

$$\beta = 1/T$$

$$\Delta\mu = \mu_R - \mu_L$$

$$\Delta\beta = \beta_R - \beta_L$$

$$\Delta T = T_R - T_L$$

we assume  $T_L > T_R$

# Restrictions from thermodynamics

$$\begin{cases} J_\rho = L_{\rho\rho}X_1 + L_{\rho q}X_2 \\ J_q = L_{q\rho}X_1 + L_{qq}X_2 \end{cases}$$

Let us consider the time-symmetric case

*Onsager relation:*  $L_{\rho q} = L_{q\rho}$

*Positivity of entropy production:*

$$\frac{d\rho}{dt} = J_\rho X_1 + J_q X_2 \geq 0$$

$$L_{\rho\rho} \geq 0, \quad L_{qq} \geq 0, \quad \det \mathbf{L} \geq 0$$

# Onsager and transport coefficients

$$G = \left( \frac{J_\rho}{\Delta\mu/e} \right)_{\Delta T=0} \Rightarrow G = \frac{e^2}{T} L_{\rho\rho}$$

$$\Xi = \left( \frac{J_q}{\Delta T} \right)_{J_\rho=0} \Rightarrow \Xi = \frac{1}{T^2} \frac{\det \mathbf{L}}{L_{\rho\rho}}$$

$$S = \left( \frac{\Delta\mu/e}{\Delta T} \right)_{J_\rho=0} \Rightarrow S = -\frac{1}{eT} \frac{L_{\rho q}}{L_{\rho\rho}}$$

Note that the positivity of entropy production implies that the (isothermal) electric conductance  $G > 0$  and the thermal conductance  $\Xi > 0$

## Seebeck and Peltier coefficients

$$S = \left( \frac{\Delta\mu/e}{\Delta T} \right)_{J_\rho=0} \Rightarrow S = -\frac{1}{eT} \frac{L_{\rho q}}{L_{\rho\rho}}$$

$$\Pi = \left( \frac{J_q}{eJ_\rho} \right)_{\Delta T=0} = \frac{L_{q\rho}}{eL_{\rho\rho}} = \frac{L_{\rho q}}{eL_{\rho\rho}} = TS$$

Seebeck and Peltier coefficients are trivially related by Onsager reciprocal relations (when time symmetry is not broken)

## Local equilibrium

Under the assumption of local equilibrium we can write phenomenological equations with  $\nabla T$  and  $\nabla \mu$  rather than  $\Delta T$  and  $\Delta \mu$

In this case we connect Onsager coefficients to **electric and thermal conductivity** rather than to conductances

$$\sigma = \left( \frac{J_\rho}{\nabla \mu / e} \right)_{\nabla T = 0}, \quad \kappa = \left( \frac{J_q}{\nabla T} \right)_{J_\rho = 0}$$

# Kinetic equations in terms of transport coefficients

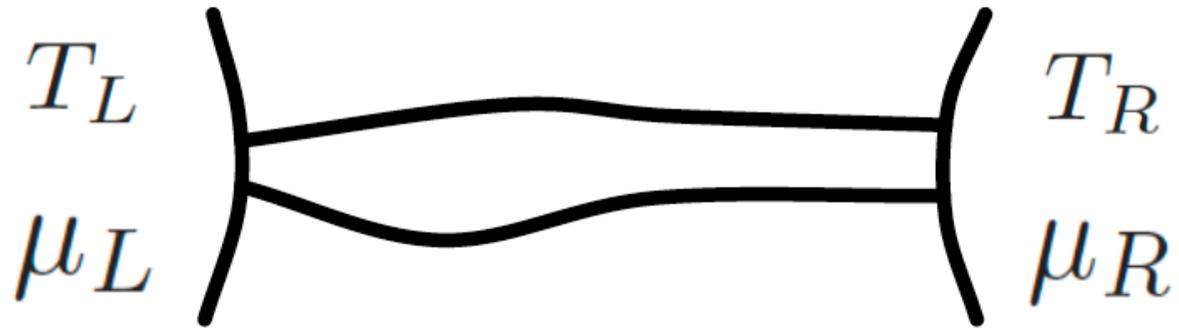
$$\begin{cases} J_\rho = -\frac{\sigma}{e^2} \nabla \mu - \frac{\sigma S}{e} \nabla T, \\ J_q = -(\kappa + T\sigma S^2) \nabla T - \frac{T\sigma S}{e} \nabla \mu, \end{cases}$$

By eliminating  $\nabla \mu$  we obtain

$$J_s = \frac{J_q}{T} = eS J_\rho - \frac{\kappa}{T} \nabla T$$

The Seebeck coefficient can be understood as the entropy transported (per unit charge) by the electron flow. The last term is independent of the particle flow

# Energy and heat representations



$$\left\{ \begin{array}{l} J_\rho = L_{\rho\rho}X_1 + L_{\rho q}X_2 \\ J_q = L_{q\rho}X_1 + L_{qq}X_2 \end{array} \right. \quad \left\{ \begin{array}{l} J_\rho = \tilde{L}_{\rho\rho}\tilde{X}_1 + \tilde{L}_{\rho u}\tilde{X}_2 \\ J_u = \tilde{L}_{u\rho}\tilde{X}_1 + \tilde{L}_{uu}\tilde{X}_2 \end{array} \right.$$

$$X_1 = -\beta\Delta\mu$$

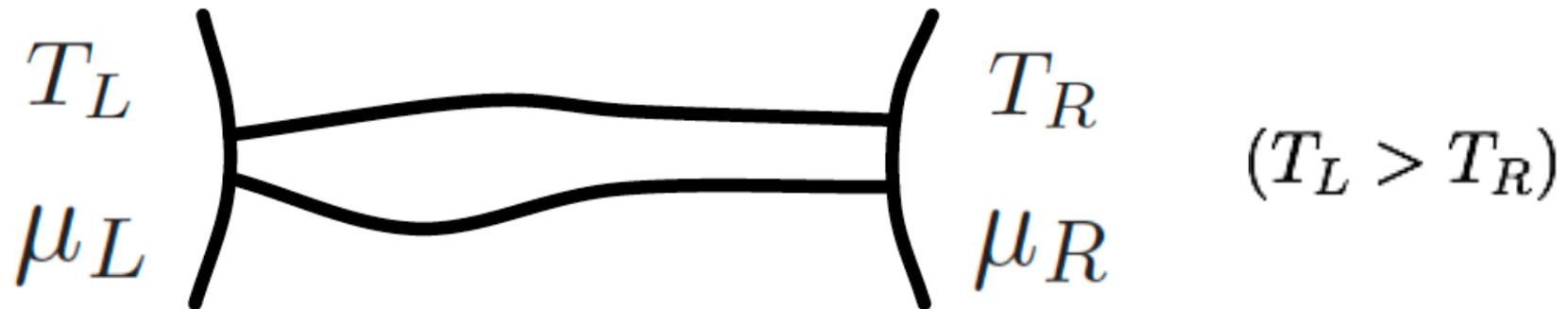
$$X_2 = \Delta\beta \approx -\Delta T/T^2$$

$$\tilde{X}_1 = -\Delta(\beta\mu)$$

$$\tilde{X}_2 = X_2$$

$$J_q = T J_s = J_u - \mu J_\rho$$

# Steady state power generation efficiency



$$\eta = \frac{W}{Q_L} = \frac{\dot{W}}{\dot{Q}_L} = \frac{J_\rho \Delta\mu}{J_q}$$

$$(\Delta\mu = \mu_R - \mu_L > 0, J_\rho > 0, J_q > 0)$$

$$\eta \leq \eta_C = \frac{T_L - T_R}{T_L} \quad (\eta_C \text{ Carnot efficiency})$$

## Maximum efficiency

$$\eta = \frac{\Delta\mu J_\rho}{J_q} = \frac{-TX_1(L_{\rho\rho}X_1 + L_{\rho q}X_2)}{L_{q\rho}X_1 + L_{qq}X_2}$$

Find the maximum of  $\eta$  over  $X_1$ , for fixed  $X_2$  (i.e., over the applied voltage  $\Delta V$  for fixed temperature difference  $\Delta T$ )

Maximum achieved for 
$$X_1 = \frac{L_{qq}}{L_{q\rho}} \left( -1 + \sqrt{\frac{\det L}{L_{\rho\rho}L_{qq}}} \right) X_2$$

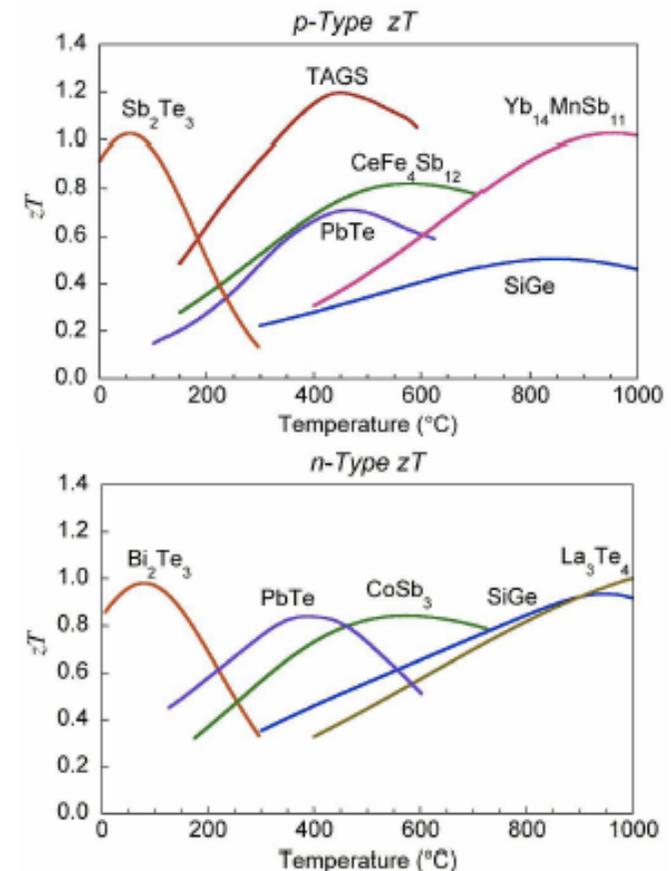
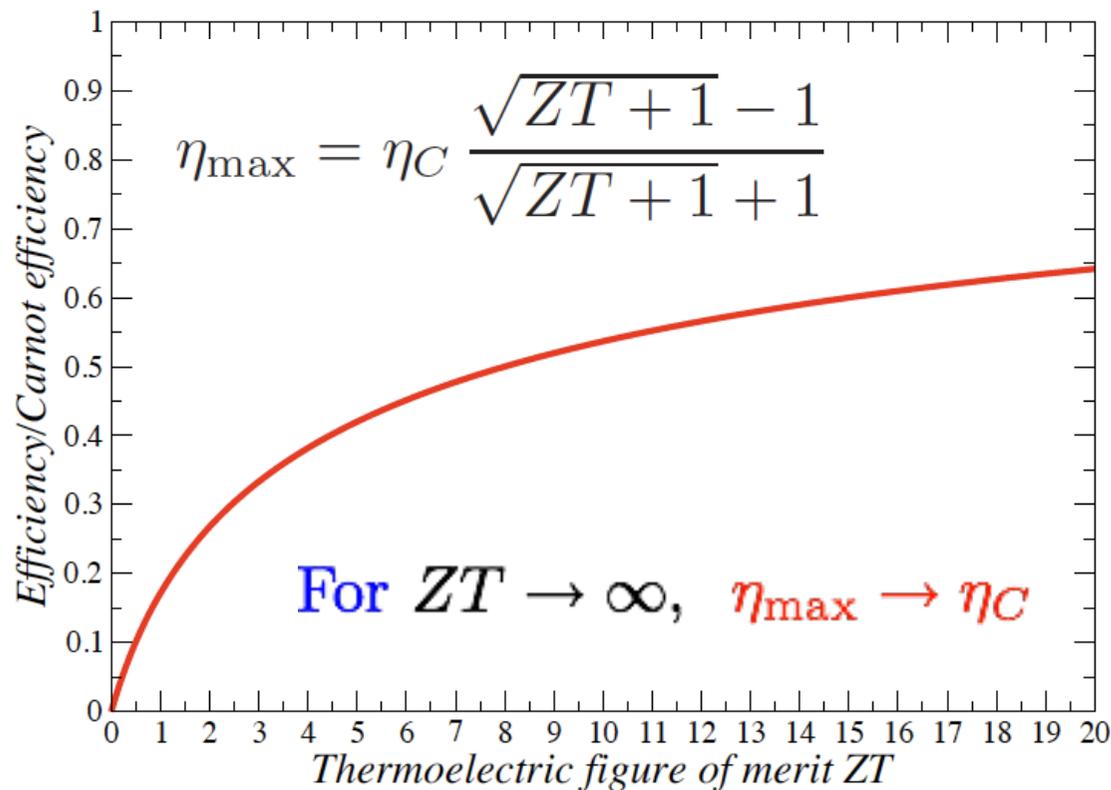
Maximum efficiency (for system with time-reversal symmetry)

$$\eta_{\max} = \eta_C \frac{\sqrt{ZT + 1} - 1}{\sqrt{ZT + 1} + 1}$$

# Thermoelectric figure of merit

$$ZT = \frac{L_{q\rho}^2}{\det \mathbf{L}} = \frac{\sigma S^2}{k} T$$

Positivity of entropy production implies  $ZT > 0$



**$ZT$  diverges iff the Onsager matrix is ill-conditioned, that is, the condition number:**

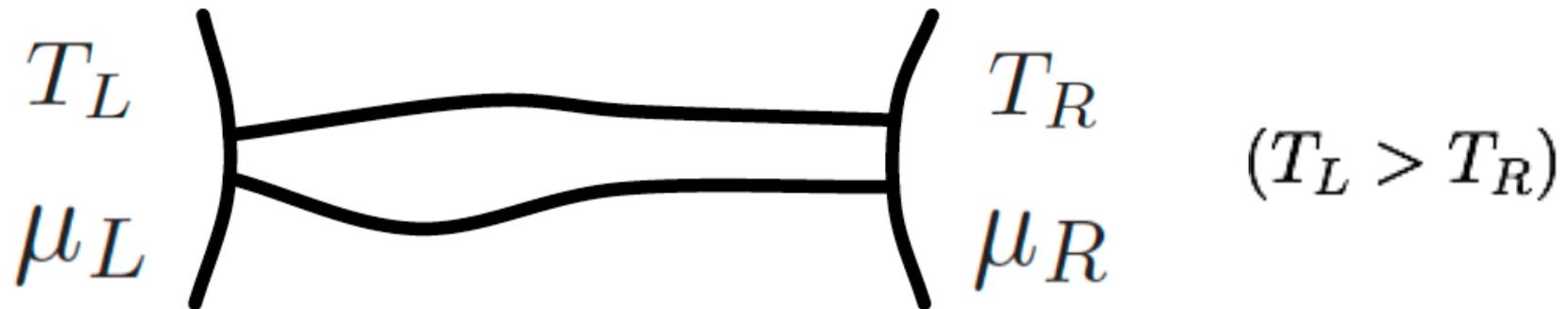
$$\text{cond}(\mathbf{L}) \equiv \frac{[\text{Tr}(\mathbf{L})]^2}{\det(\mathbf{L})} \quad \text{diverges}$$

**In such case the system is singular (strong-coupling limit):**

$$J_q \propto J_\rho$$

**(the ratio  $J_q/J_\rho$  is independent of the applied voltage and temperature gradients)**

# Maximum refrigeration efficiency



$$\eta^{(r)} = \frac{J_q}{\dot{W}} \quad (J_q < 0, \dot{W} < 0)$$

$$\eta_{\max}^{(r)} = \eta_C \frac{\sqrt{ZT + 1} - 1}{\sqrt{ZT + 1} + 1}$$

$ZT$  is the figure of merit also for refrigeration

# Finite time thermodynamics

Carnot efficiency obtained in the limit of quasi-static (reversible) processes, so that the extracted power reduces to zero.

$$\omega \equiv \dot{W} = J_{\rho} \Delta\mu \rightarrow 0 \quad \text{for} \quad ZT \rightarrow \infty$$

Finite time thermodynamics (endoreversible thermodynamics) considers finite time (Carnot) cycles; the efficiency at the maximum output power is an important concept

## Efficiency at maximum power

For finite time Carnot cycles the efficiency at the maximum output power is given (under some conditions) by the so-called **Curzon-Ahlborn efficiency** (Chambadal-Novikov efficiency)

Reservoir temperatures  $T_{\text{hot}}, T_{\text{cold}}$

Isothermal transformations: working fluid at  $T_{\text{warm}}, T_{\text{tepid}}$

Heat flow rate proportional to the temperature difference

$$\frac{|Q_{\text{hot}}|}{t_{\text{hot}}} = \sigma_{\text{hot}}(T_{\text{hot}} - T_{\text{warm}}); \quad \frac{|Q_{\text{cold}}|}{t_{\text{cold}}} = \sigma_{\text{cold}}(T_{\text{tepid}} - T_{\text{cold}})$$

$$t_{\text{cycle}} \approx t_{\text{hot}} + t_{\text{cold}}$$

# Curzon-Ahlborn efficiency

Optimum power delivered by the engine:

$$\omega_{\max} = \sigma_{\text{hot}} \sigma_{\text{cold}} \left[ \frac{\sqrt{T_{\text{hot}}} - \sqrt{T_{\text{cold}}}}{\sqrt{\sigma_{\text{hot}}} + \sqrt{\sigma_{\text{cold}}}} \right]^2$$

Efficiency at the maximum output power is given by the **Curzon-Ahlborn efficiency**

$$\eta_{CA} = 1 - \sqrt{\frac{T_{\text{cold}}}{T_{\text{hot}}}}$$

The CA efficiency is not a generic bound for the efficiency at maximum power; yet it describes the efficiency of actual thermal plants quite well

(see M. Esposito *et al.* PRL **105**, 150603 (2010))

# Linear response Curzon-Ahlborn upper bound

The CA efficiency is a universal upper bound within linear response

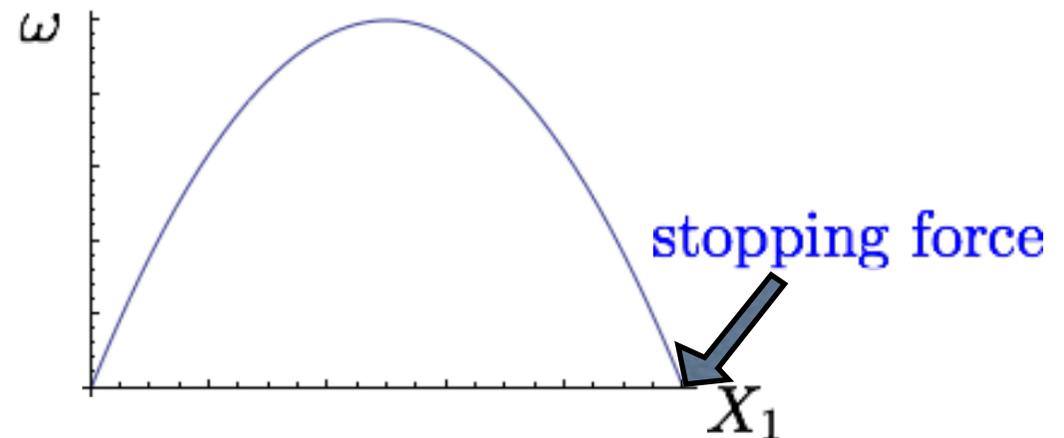
$$\eta_{CA} = \frac{\eta_C}{2} + O(\eta_C^2)$$

Within **linear response**, the output power

$$\omega = J_\rho \Delta\mu = -J_\rho T X_1 = -L_{\rho\rho} T X_1^2 - L_{\rho q} T X_1 X_2$$

is maximum when

$$X_1 = -\frac{L_{\rho q}}{2L_{\rho\rho}} X_2$$



## Maximum output power

$$\omega_{\max} = \frac{T}{4} \frac{L_{\rho q}^2}{L_{\rho\rho}} X_2^2 = \frac{\eta_C}{4} \frac{L_{\rho q}^2}{L_{\rho\rho}} X_2^2$$

## Efficiency at maximum power

$$\eta(\omega_{\max}) = \frac{\eta_C}{2} \frac{ZT}{ZT + 2}$$

Both maximum efficiency and efficiency at maximum power are monotonous growing functions of the thermoelectric figure of merit  $ZT$

$$\eta(\omega_{\max}) \rightarrow \eta_{CA} = \frac{\eta_C}{2} \text{ when } ZT \rightarrow \infty$$

# Non-interacting systems, Landauer-Büttiker formalism

## Charge current

$$J_e = eJ_\rho = \frac{e}{h} \int_{-\infty}^{\infty} dE \tau(E) [f_L(E) - f_R(E)]$$

## Heat current from reservoir $\alpha$

$$J_{q,\alpha} = \frac{1}{h} \int_{-\infty}^{\infty} dE (E - \mu_\alpha) \tau(E) [f_L(E) - f_R(E)]$$

$\tau(E)$  transmission probability for a particle with energy  $E$

$f_\alpha(E)$  Fermi distribution of the particles injected from reservoir  $\alpha$

# Onsager coefficients

The Onsager coefficients are obtained from the linear expansion of the charge and thermal currents

$$L_{\rho\rho} = e^2 T I_0, \quad L_{\rho q} = L_{q\rho} = e T I_1, \quad L_{qq} = T I_2$$

$$I_n = \frac{1}{h} \int_{-\infty}^{\infty} dE (E - \mu)^n \tau(E) \left( -\frac{\partial f}{\partial E} \right)$$

## Wiedemann-Franz law

Phenomenological law: the ratio of the thermal to the electrical conductivity of a great number of metals is directly proportional to the temperature, with a proportionality factor which is to a good accuracy the same for all metals.

$$\frac{\kappa}{\sigma} = \mathcal{L}T$$

Lorenz number

$$\mathcal{L} = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2$$

## Sommerfeld expansion

The Wiedemann-Franz law can be derived for low-temperature non-interacting systems both within kinetic theory or Landauer-Büttiker approaches

In both cases it is substantiated by Sommerfeld expansion

$$J_{q,\alpha} = \frac{1}{h} \int_{-\infty}^{\infty} dE (E - \mu_{\alpha}) \tau(E) [f_L(E) - f_R(E)]$$

$$J_e = eJ_{\rho} = \frac{e}{h} \int_{-\infty}^{\infty} dE \tau(E) [f_L(E) - f_R(E)]$$

We assume smooth transmission functions  $\tau(E)$  in the neighborhood of  $E=\mu$

To lowest order in  $k_B T/E_F$

$$G = \left. \frac{eJ_e}{\Delta\mu} \right|_{\Delta T=0} = \frac{e^2}{h} \int_{-\infty}^{\infty} dE \tau(E) \left( -\frac{\partial f}{\partial E} \right) \approx \frac{e^2}{h} \tau(\mu)$$

Assuming  $L_{\rho\rho}L_{qq} \gg (L_{\rho q})^2$

$$\Xi = \left. \frac{J_q}{\Delta T} \right|_{J_e=0} = \frac{L_{\rho\rho}L_{qq} - L_{\rho q}^2}{L_{\rho\rho}T^2} \approx \frac{L_{qq}}{T^2}$$

To the leading order (second order) in  $k_B T/E_F$

$$\frac{L_{qq}}{T^2} = \frac{1}{hT} \int_{-\infty}^{\infty} dE \tau(E) (E - \mu)^2 \left( -\frac{\partial f}{\partial E} \right) \approx \frac{\pi^2}{3} k_B^2 \frac{T}{h} \tau(\mu)$$

Wiedemann-Franz law:

$$\frac{\Xi}{GT} = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 = \mathcal{L}$$

# Wiedemann-Franz law and thermoelectric efficiency

$$ZT = \frac{GT}{\Xi} S^2 = \frac{S^2}{\mathcal{L}}$$

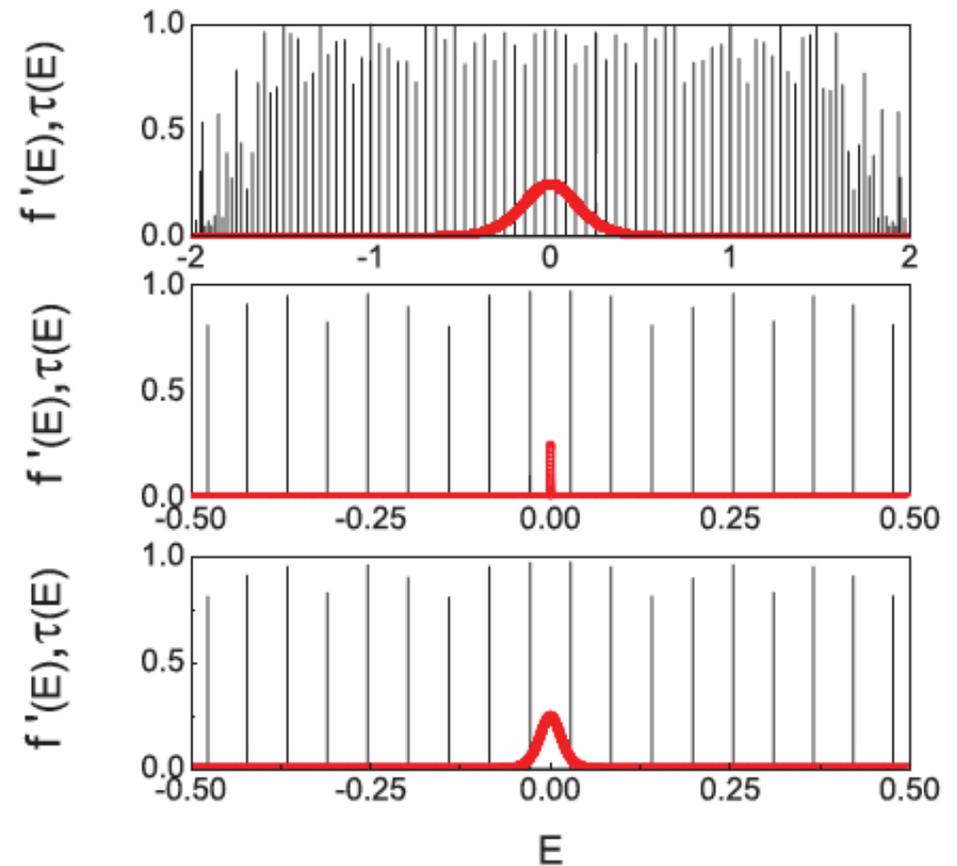
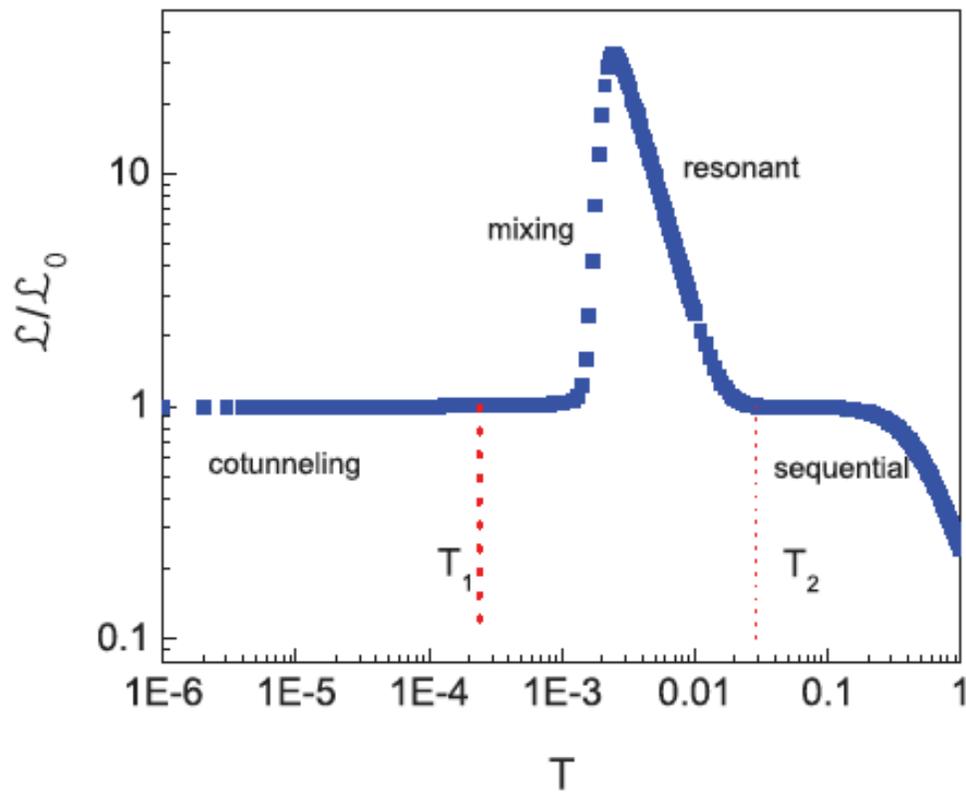
Wiedemann-Franz law derived under the condition  $L_{\rho\rho}L_{qq} \gg (L_{\rho q})^2$  and therefore

$$ZT = \frac{L_{\rho q}^2}{\det \mathbf{L}} \approx \frac{L_{\rho q}^2}{L_{\rho\rho}L_{qq}} \ll 1$$

Wiedemann-Franz law violated in

- low-dimensional interacting systems that exhibit non-Fermi liquid behavior
- small systems where transmission can show significant energy dependence

# (Violation of) Wiedemann-Franz law in small systems



(Bosisio, Balachandran, Benenti, PRB **86**, 035433 (2012);  
see also Vavilov and Stone, PRB **72**, 205107 (2005))

# Cutler-Mott formula

For non-interacting electrons

$$S = -\frac{1}{T} \frac{L_{\rho q}}{L_{\rho\rho}} = \frac{1}{eT} \frac{\int dE \tau(E) (E - \mu) \left(-\frac{\partial f}{\partial E}\right)}{\int dE \tau(E) \left(-\frac{\partial f}{\partial E}\right)}$$

Consider smooth transmissions  $\tau(E) \approx \tau(\mu) + \tau'(\mu)(E - \mu)$

$$S \approx \frac{\pi^2 k_B^2 T}{3e} \frac{\tau'(\mu)}{\tau(\mu)} = \frac{\pi^2 k_B^2 T}{3e} \left. \frac{d \ln G(E)}{dE} \right|_{E=\mu}$$

Electron and holes contribute with opposite signs: we want **sharp, asymmetric transmission functions** to have large thermopowers (ex: resonances, Anderson QPT, see Imry and Amir, 2010), violation of WF, large ZT.

# Thermoelectric efficiency

$$\eta = \frac{[(\mu_R - \mu_L)/e]J_e}{J_{qL}} = \frac{(\mu_R - \mu_L) \int_{-\infty}^{\infty} dE \tau(E) [f_L(E) - f_R(E)]}{\int_{-\infty}^{\infty} dE (E - \mu_L) \tau(E) [f_L(E) - f_R(E)]}$$

**If transmission is possible only inside a tiny energy window around  $E=E_*$  then**

$$\eta = \frac{\mu_L - \mu_R}{E_* - \mu_L}$$

## Energy filtering mechanism

In the limit  $J_\rho \rightarrow 0$ , corresponding to reversible transport

$$\frac{E_\star - \mu_L}{T_L} = \frac{E_\star - \mu_R}{T_R} \Rightarrow E_\star = \frac{\mu_R T_L - \mu_L T_R}{T_L - T_R}$$

$$\eta = \eta_C = 1 - T_R/T_L \quad \text{Carnot efficiency}$$

Carnot efficiency obtained in the limit of reversible transport (zero entropy production) and zero output power

[Mahan and Sofo, PNAS 93, 7436 (1996);  
Humphrey et al., PRL 89, 116801 (2002)]

# Interacting systems, Green-Kubo formula

The Green-Kubo formula expresses linear response transport coefficients in terms of dynamic correlation functions of the corresponding current operators, calculated at thermodynamic equilibrium

$$L_{ij} = \lim_{\omega \rightarrow 0} \text{Re} L_{ij}(\omega)$$

$$L_{ij}(\omega) = \lim_{\epsilon \rightarrow 0} \int_0^{\infty} dt e^{-i(\omega - i\epsilon)t} \lim_{\Lambda \rightarrow \infty} \frac{1}{\Lambda} \int_0^{\beta} d\tau \langle J_i J_j(t + i\tau) \rangle_T$$

$$\text{Re} L_{ij}(\omega) = \mathcal{D}_{ij} \delta(\omega) + L_{ij}^{\text{reg}}(\omega)$$

Non-zero generalized Drude weights signature of ballistic transport

# Conservation laws and thermoelectric efficiency

Suzuki's formula for finite-size Drude weights

$$D_{ij}(\Lambda) \equiv \frac{1}{2\Lambda} \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt' \langle J_i(t') J_j(0) \rangle_T = \frac{1}{2\Lambda} \sum_{n=1}^M \frac{\langle J_i Q_n \rangle_T \langle J_j Q_n \rangle_T}{\langle Q_n^2 \rangle_T}$$

$Q_n$  relevant (i.e., non-orthogonal to charge and thermal currents), mutually orthogonal conserved quantities

$$\mathcal{D}_{ij} = \lim_{t \rightarrow \infty} \lim_{\Lambda \rightarrow \infty} \frac{1}{2\Lambda t} \int_0^t dt' \langle J_i(t') J_j(0) \rangle_T$$

# Momentum-conserving systems

Consider systems with a single relevant constant of motion, notably momentum

Ballistic contribution to  $\det(L)$  vanishes as

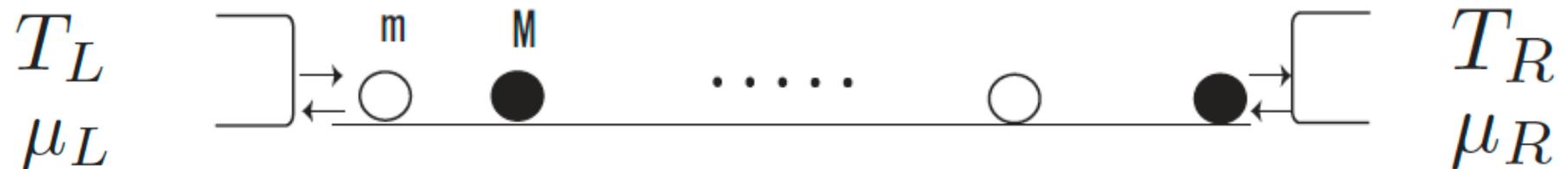
$$\mathcal{D}_{\rho\rho}\mathcal{D}_{uu} - \mathcal{D}_{\rho u}^2 = 0$$

Therefore thermal conductivity grows subballistically, while the charge conductivity grows ballistically and the thermopower is size-independent, so that the figure of merit diverges at the thermodynamic limit

(Benenti, Casati, Jiao, preprint)

# Example: 1D interacting classical gas

Consider a **one dimensional gas** of elastically colliding particles with **unequal masses:  $m, M$**



For  $M = m$   $J_u = T_L \gamma_L - T_R \gamma_R$  ( $J_u = J_q + \mu J_\rho$ )

$J_\rho = \gamma_L - \gamma_R$  **ZT = 1**

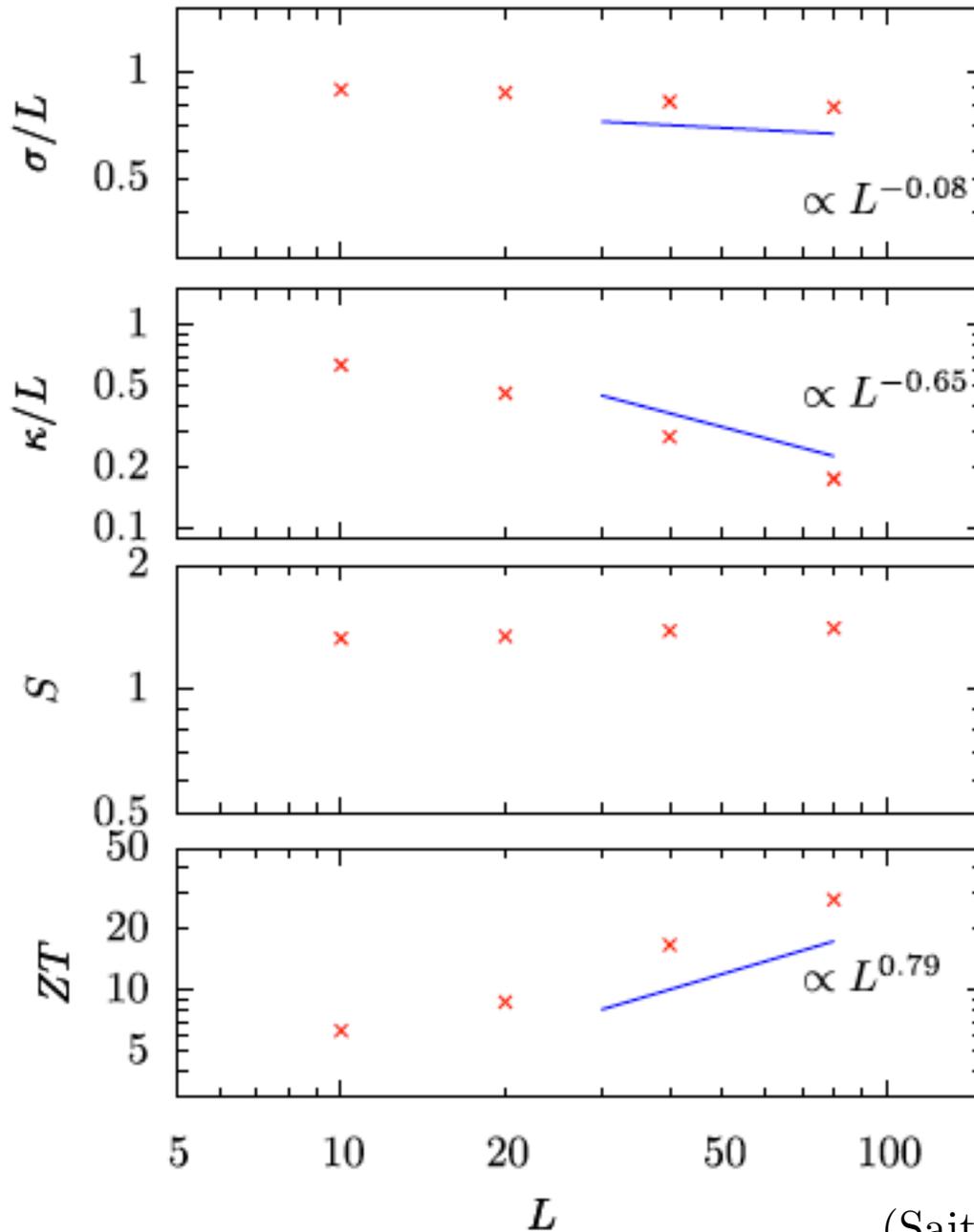
$\gamma_\alpha = \frac{1}{h\beta_\alpha} e^{\beta_\alpha \mu_\alpha}$  injection rates

For  $M \neq m$  ZT depends on the system size

# Anomalous thermal transport

$$ZT = \frac{\sigma S^2}{k} T$$

$ZT$  diverges  
increasing the systems size



(Saito, G.B., Casati, Chem. Phys. **375**, 508 (2010))