# Transport in strongly correlated systems

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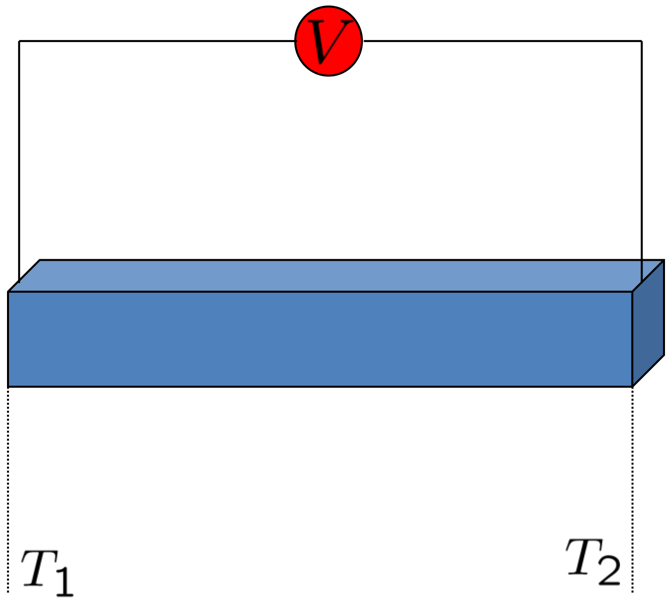
**Lecture 3: Transport with strong interactions**

- Thermopower, Lorenz number, figure of merit
- Hubbard model in the atomic limit
- Comparison to experimental data
- Single molecules with strong interactions




Thermopower: $S = \frac{V}{T_2 - T_1}$

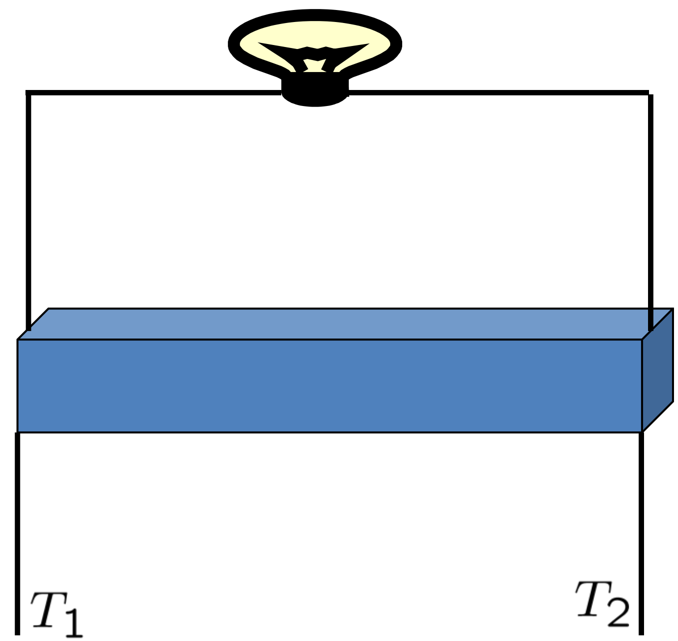
$\eta =$ Conversion efficiency

$$\eta = \eta_{\text{Carnot}} \times f(ZT)$$

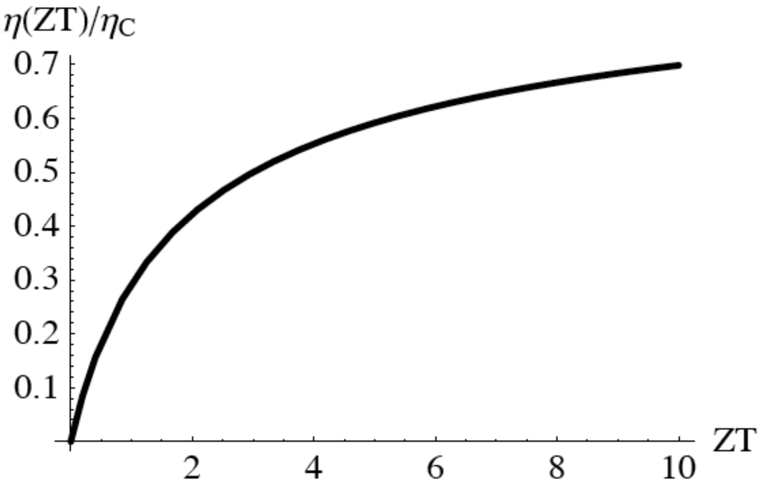
$$ZT \uparrow \Rightarrow \eta \uparrow$$

$$ZT = \infty \Rightarrow \eta = \eta_{\text{Carnot}}$$

Thermoelectric battery



$$ZT = \frac{TS^2\sigma}{\kappa}$$




- $S$ - thermopower
- $\sigma$ - electrical conductivity
- $\kappa$ - thermal conductivity

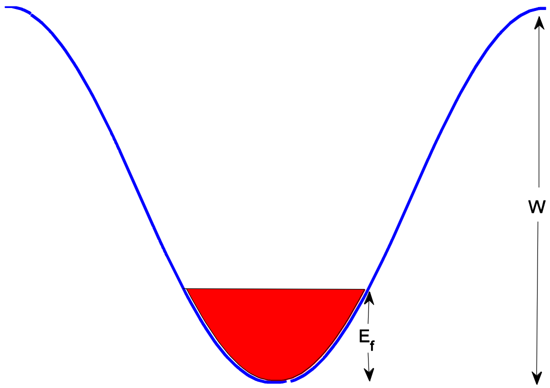
$$\kappa = \kappa_e + \kappa_{ph}$$

electron
(or hole etc.)

phonon

How big is $ZT$ "typically"?

Typical "degenerate" metal ($E_F \gg k_B T$)




$$S \sim \frac{k_B}{e}\frac{k_B T}{E_f} \text{ (Mott formula)}$$

$$\kappa_{\text{ph}} \ll \kappa_e \text{ (at 300 K)}$$

$$L = \frac{\kappa}{T\sigma} \sim \left(\frac{k_B}{e}\right)^2$$

[Wiedemann-Franz (WF) law]

$$ZT \sim \left(\frac{k_B T}{E_F}\right)^2 \ll 1$$

Decreasing $E_F$ increases $ZT$ Eventually $\kappa_{ph} \sim \kappa$

Typically $S$ and $\sigma$ change in opposite ways with tunable parameters (carrier density, effective mass etc.)

Maximize $TS^2\sigma$ or minimize $\kappa_{ph}$ to maximize $ZT$

Limiting $ZT = \frac{TS^2\sigma}{\kappa_e}$

If $E_F$ is continuously decreased and $\kappa_{ph}$ can be ignored what is the limiting $ZT$?

Eventually $E_f \ll k_B T$ (completely non-degenerate metal)

$$S \sim \frac{k_B}{e}$$

with a log dependence on carrier concentration and temperature

$$L \sim \left(\frac{k_B}{e}\right)^2$$

(Classical WF law)

$$ZT \sim 1$$

Can we do better?

Yes, if $k_B T \gg W$ (the bandwidth)

Again, if $\kappa_{ph} = 0$

$$S \sim \frac{k_B}{e}$$

but $L = \# \left(\frac{k_B}{e}\right)^2 \left(\frac{W}{T}\right)^2$ (Violation of WF law)

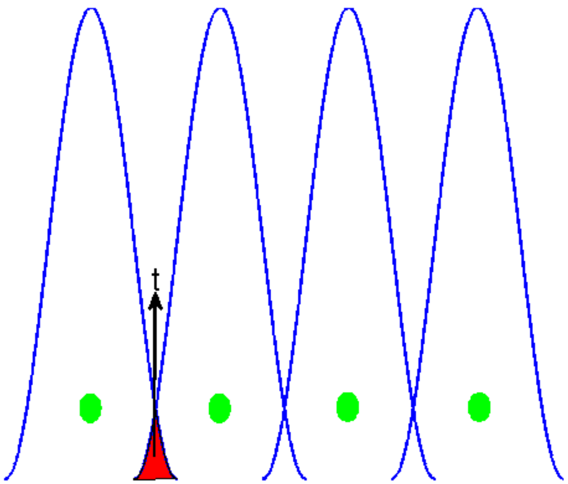
since $\kappa \sim C_v$ and $C_v \sim \frac{W^2}{T^2}$

Thus $ZT \gg 1$

$\kappa_e$ does not limit $ZT$ if $\kappa_{ph}$ can be reduced indefinitely

What materials if any are likely to have small $W$?

# Complex oxides with $d$ of $f$ orbital bands




but narrow bands $\Rightarrow$ strong correlations

Can unusual thermoelectric behavior survive strong correlation effects?

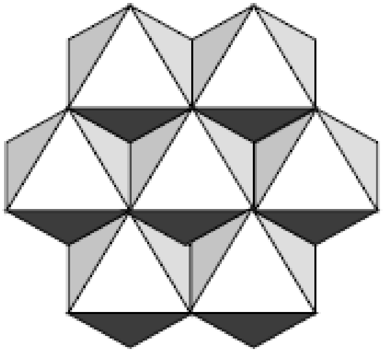
Yes. [S. Mukerjee and J. E. Moore, *Appl. Phys. Lett.* **90** 112107 (2007)]

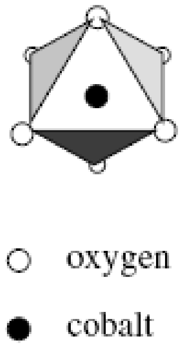
Real material $Na_xCoO_2$

Single particle hopping $\frac{t}{k_B} \sim 100K$ + strong correlations

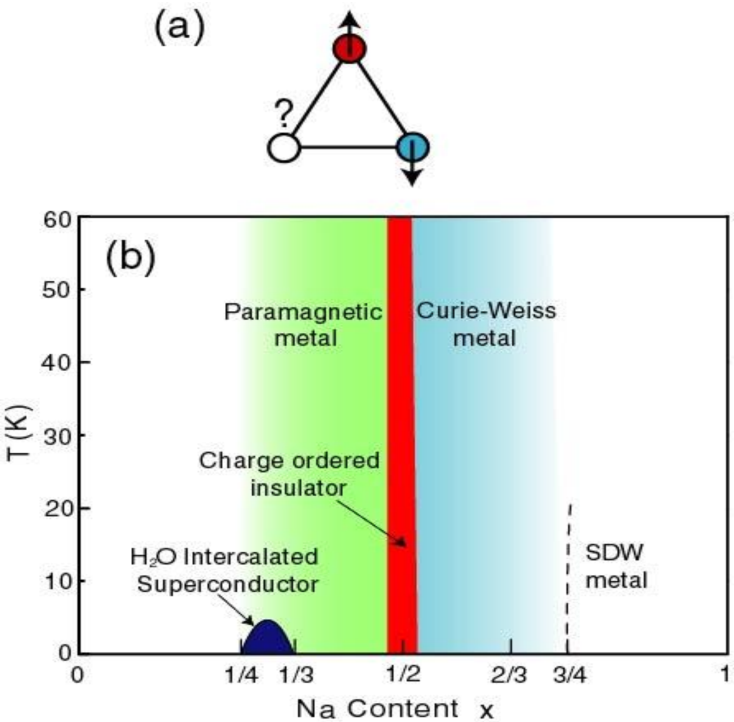
[M. Z. Hasan *et. al.*, *Phys. Rev. Lett.* **92** 246402 (2005)]

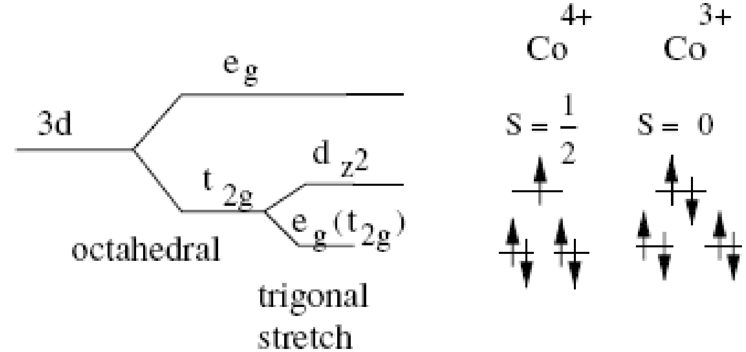
# $Na_xCoO_2$






Triangular lattice of Co ions surrounded by octahedron of O ions



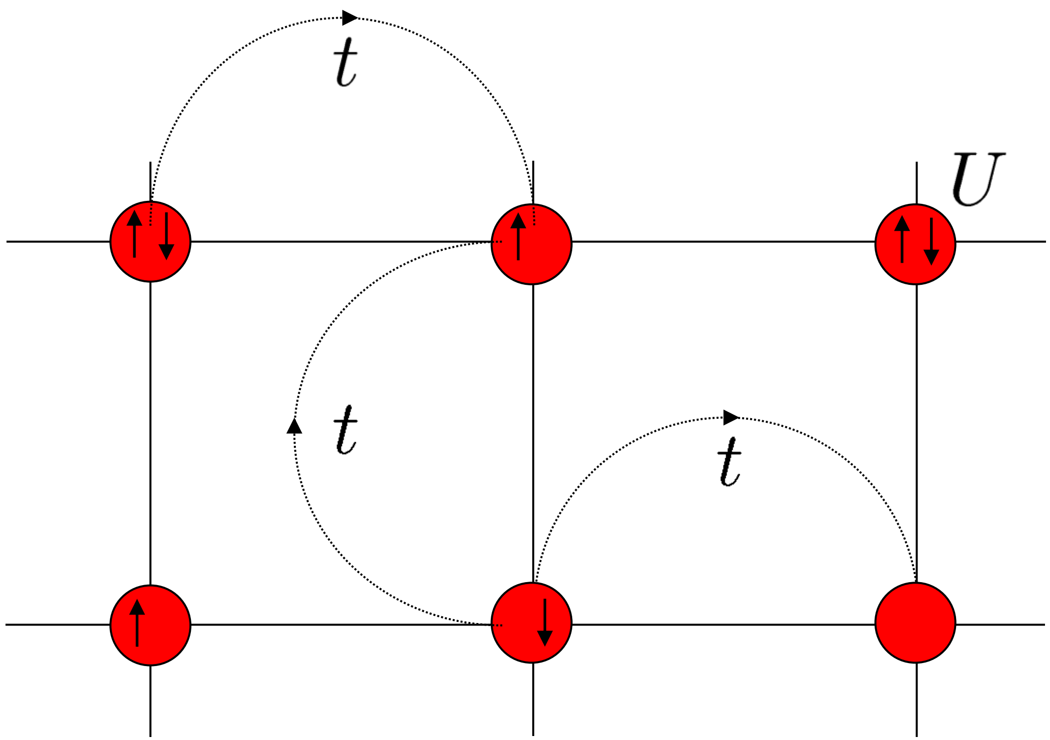

$CoO_2$-Mott insulator with $Co^{4+}$

Na produces $Co^{3+}$

Electron doping

# Hubbard model

$$H = -t \sum_{\langle ij \rangle, \sigma} \left( c^{\dagger}_{i\sigma} c_{j\sigma} + c^{\dagger}_{j\sigma} c_{i\sigma} \right) + U \sum_{i\sigma} n_{i\uparrow} n_{i\downarrow}$$



$$\hat{J}_x = \frac{eat}{i\hbar} \sum_{j,\sigma} \left( c^\dagger_{j\sigma} c_{j+\hat{x}\sigma} - c^\dagger_{j+\hat{x}\sigma} c_{j\sigma} \right)$$

$$\begin{aligned} \hat{J}^Q_x \quad &= \quad \frac{Uat}{i\hbar} \sum_{j,\sigma} n_{j-\sigma} \left( c^\dagger_{j\sigma} c_{j+\hat{x}\sigma} - c^\dagger_{j+\hat{x}\sigma} c_{j\sigma} \right) \\ &+ \frac{at^2}{i\hbar} \sum_{\langle jl \rangle,\sigma} \hat{\delta}_l . \hat{x} \left( c^\dagger_{j\sigma} c_{l\sigma} - c^\dagger_{l\sigma} c_{j\sigma} \right) - \frac{\mu}{e} \hat{J}_x \end{aligned}$$

$$\dot{\hat{n}} = -\frac{i}{\hbar} \left[ \hat{n}, \hat{H} \right] = -\nabla . \hat{\mathbf{J}}$$

$$\dot{\hat{h}} = -\frac{i}{\hbar} \left[ \hat{h}, \hat{H} \right] = -\nabla . \hat{\mathbf{J}}^E$$

$$\hat{\mathbf{J}}^Q = \hat{\mathbf{J}}^E - \mu \hat{\mathbf{J}}$$

$$\boxed{\begin{aligned} J_\alpha &= -N^{11}_{\alpha\beta}\nabla_\beta\bar{\mu} - N^{12}_{\alpha\beta}\nabla_\beta T \\ J^Q_\alpha &= -TN^{21}_{\alpha\beta}\nabla_\beta\bar{\mu} - \frac{N^{22}_{\alpha\beta}}{T}\nabla_\beta T \end{aligned}}$$

$$N^{11}_{\alpha\beta} = L^{11}_{\alpha\beta}$$

$$N^{12}_{\alpha\beta} = \frac{L^{12}_{\alpha\beta} - \mu L^{11}_{\alpha\beta}}{T}$$

$$N^{22}_{\alpha\beta} = L^{22}_{\alpha\beta} - \mu\left(L^{12}_{\alpha\beta} + L^{21}_{\alpha\beta}\right) + \mu^2 L^{11}_{\alpha\beta}$$

$$\boxed{N^{ab}_{\alpha\beta} = N^{ba}_{\beta\alpha}}$$

$$L^{ab}_{\alpha\beta}(\omega) = \frac{\pi\left(1 - e^{-\beta\hbar\omega}\right)}{\hbar\omega V}\int_0^\infty dt\ e^{i\omega t}\langle \hat{J}^{(b)}_\beta(t)\hat{J}^{(a)}_\alpha(0)\rangle$$

Very hard to calculate for any general values of $t$, $T$, $U$ and $n$ (filling)

For $U \ll t$, one can perturb about the non-interacting system

$T \gg (U, t)$ high temperature expansion

Perturbation theory also possible in the "atomic limit" (strong correlations)

$\boxed{t \ll (T, U)}$

$\boxed{J \ll t \ll T}$

$J \sim t^2/U$

Atomic limit $\Rightarrow H = U \sum_i n_{i\uparrow} n_{i\downarrow}$ in the exponentials in the Kubo formula

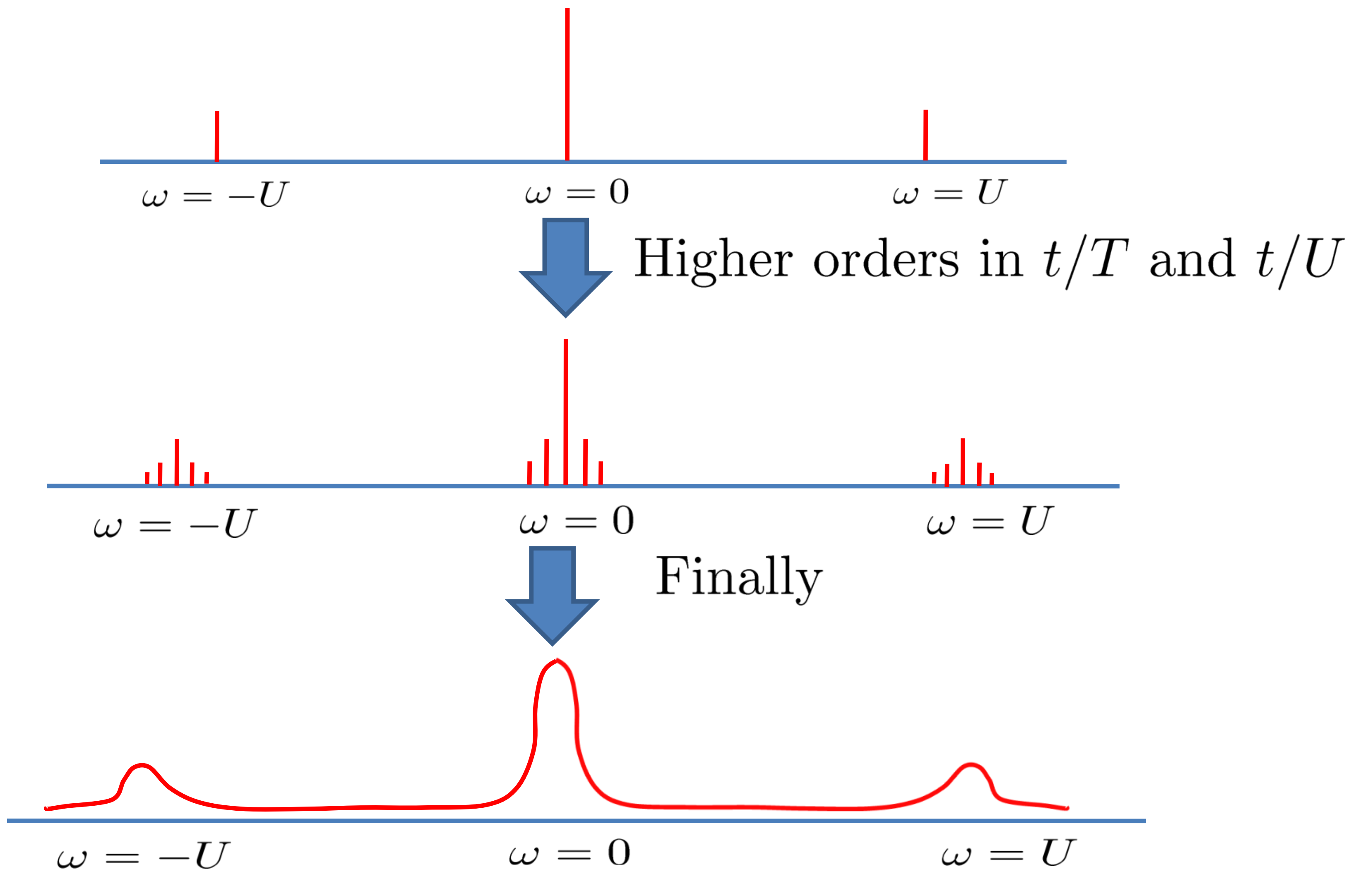
Since this $\hat{H}$ is diagonal in the site basis, it is a convenient one to evaluate traces

Kubo formula contains terms like $\langle \hat{J} \hat{J} \rangle$

Lowest order contribution in the atomic limit is thus a hop to a new site and back

$$L_{\alpha\beta} \sim t^2$$

Any conductivity $L(\omega) = A_0\delta(\omega) + A_U\delta(\omega - U) + A_{-U}\delta(\omega + U)$



$$L^{11}(\omega) = \ell^{11}\delta(\omega) + \dots$$
$$L^{12}(\omega) = \ell^{12}\delta(\omega) + \dots$$
$$L^{22}(\omega) = \ell^{22}\delta(\omega) + \dots$$

$$\left[\frac{L^{mn}(\omega)}{L^{m'n'}(\omega)}\right]_{\omega=0} = \frac{\ell^{mn}}{\ell^{m'n'}}$$

What does this mean?

$$\ell^{mn} = \int_{-\frac{\Delta\omega}{2}}^{\frac{\Delta\omega}{2}} L^{mn}(\omega)d\omega \approx L^{mn}(\omega = 0)\Delta\omega$$

$\Delta\omega$ - broadening assumed to be independent of $(mn)$

$$S = -\frac{k_B}{e}\left[\frac{\beta U e^{2\beta\mu}}{e^{\beta U}+e^{2\beta\mu}} - \beta\mu\right]$$

$$\frac{\kappa}{T\sigma} = \frac{k_B^2}{e^2}\frac{(\beta U)^2 e^{-\beta(U-4\mu)}}{e^{-\beta(U-3\mu)}+e^{\beta\mu}} + \ldots + \frac{k_B^2}{e^2}\frac{\nu t^2}{k_B^2 T^2}$$

$$e^{\beta\mu} = \frac{\rho-1+\sqrt{(\rho-1)^2+\rho(2-\rho)e^{-\beta U}}}{(2-\rho)e^{-\beta U}}$$

$\nu$, geometry dependent
$= 2d - 1$ for $d$ dimensional hypercubic lattice
$= 4$ for triangular lattice

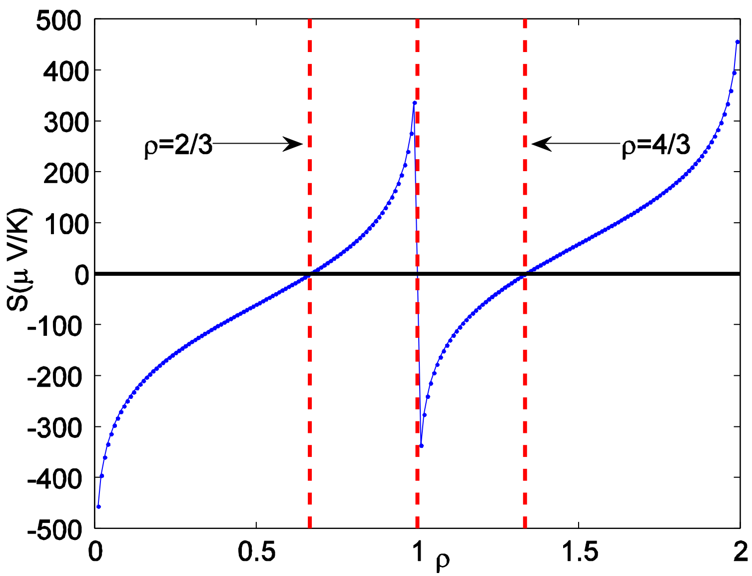
[S. Mukerjee and J. E. Moore, *Appl. Phys. Lett.* **90** 112107 (2007)]

[S. Mukerjee, *Phys. Rev. B* **72** 195109 (2005)]

If $U \gg k_B T$

$$S = -\frac{k_B}{e}\log\left[\frac{2(1-\rho)}{\rho}\right] \qquad \rho \leq 1 \qquad \text{(Heikes limit)}$$

$\rho$ - electron filling $\qquad S(\rho) = -S(2-\rho)$




$S$ changes sign three times

$S$ goes to $\infty$ at band $(\rho = 0, 2)$ and Mott $(\rho = 1)$ insulator

Mott insulator and sign change at $\rho = (1/3, 2/3)$, correlation effects

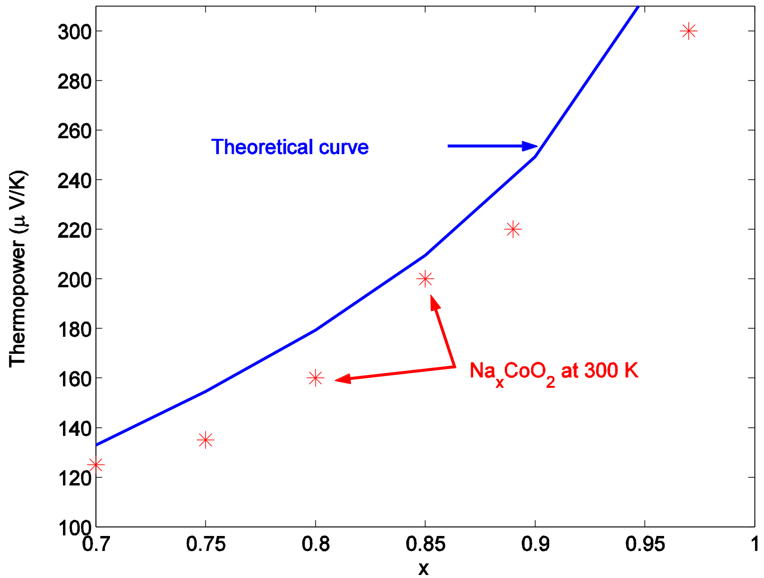
$$L = f(z)\frac{k_B^2}{e^2}\left(\frac{t}{k_B T}\right)^2$$

$z$ - lattice coordination #

Violation of Wiedemann-Franz law

[S. Mukerjee and J. E. Moore, *Appl. Phys. Lett.* **90** 112107 (2007)]

[S. Mukerjee, *Phys. Rev. B* **72** 195109 (2005)]




$$x = \rho - 1$$

Experimental data

[M. Lee *et. al.*, *Nature Materials* **5** 237 (2006)]

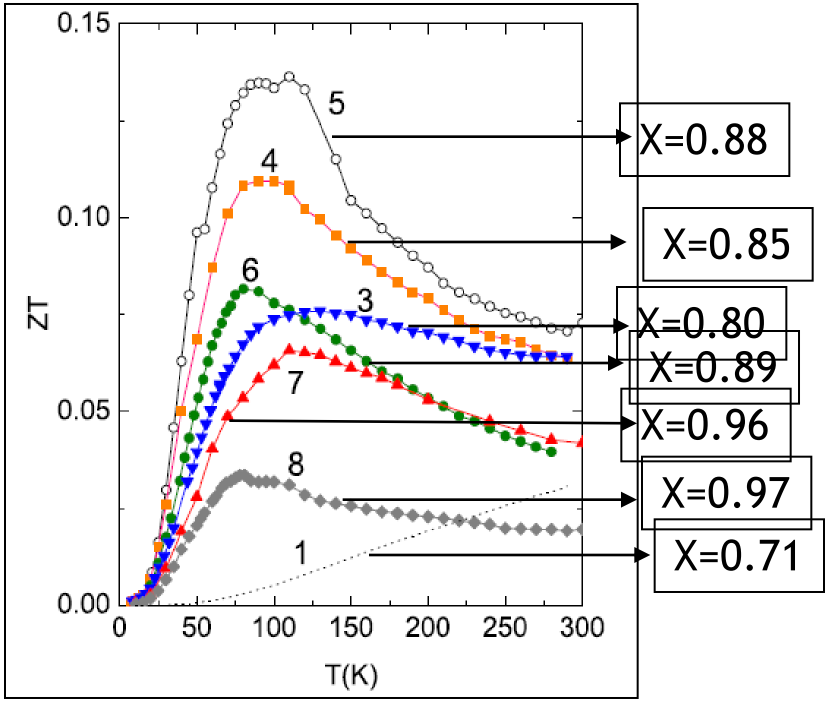
$$\sigma = \frac{A}{k_B T}\rho(1-\rho)$$

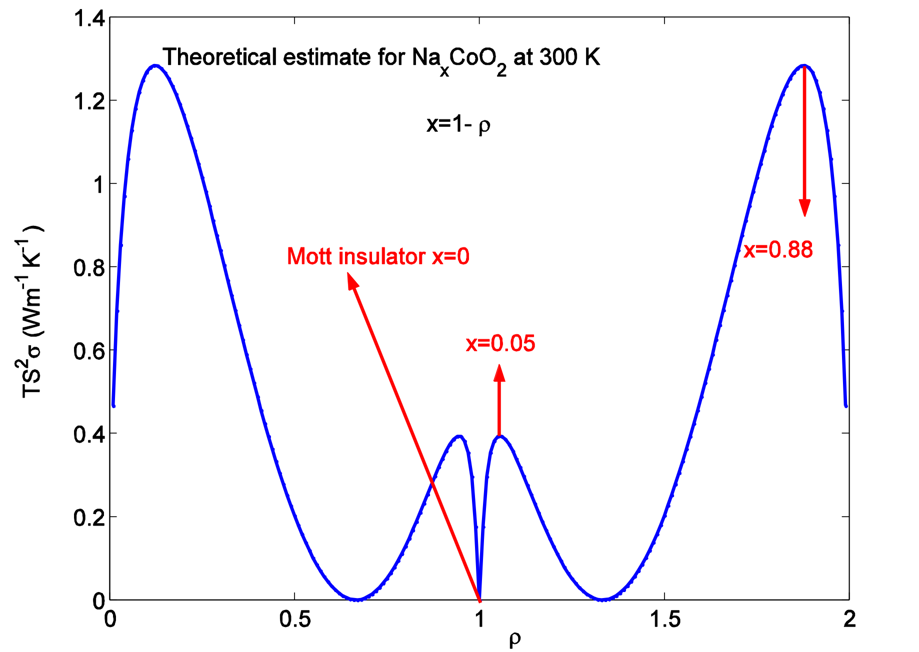
$\delta(\omega)$ broadened by hand to $\tau$ (assumed indepent of $\rho$)

$$\kappa_e = TL_e\sigma \ll \kappa_{\text{measured}}$$

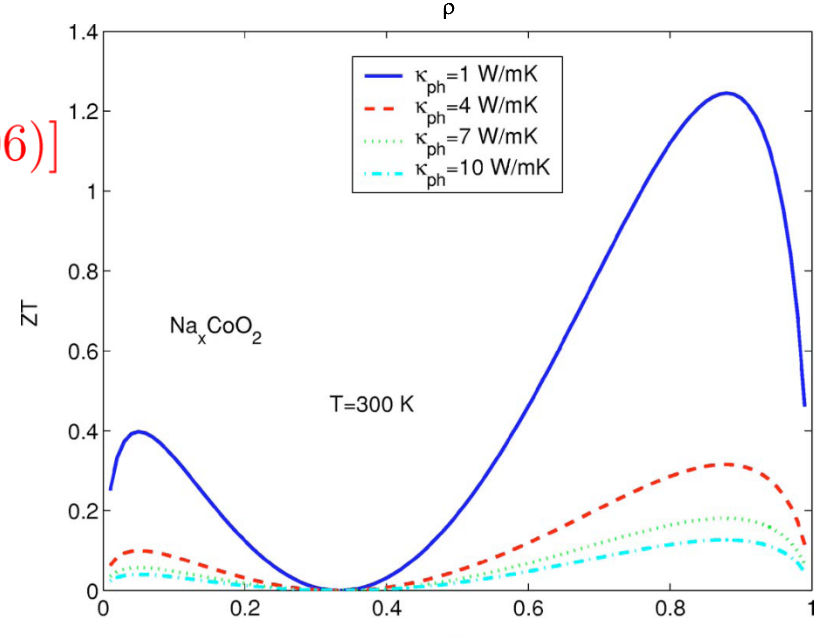
So, $\kappa_{\text{measured}} \approx \kappa_{ph}$ and $ZT = \frac{TS^2\sigma}{\kappa_{ph}}$

$\kappa_{\text{measured}}$ roughly independent of $x$



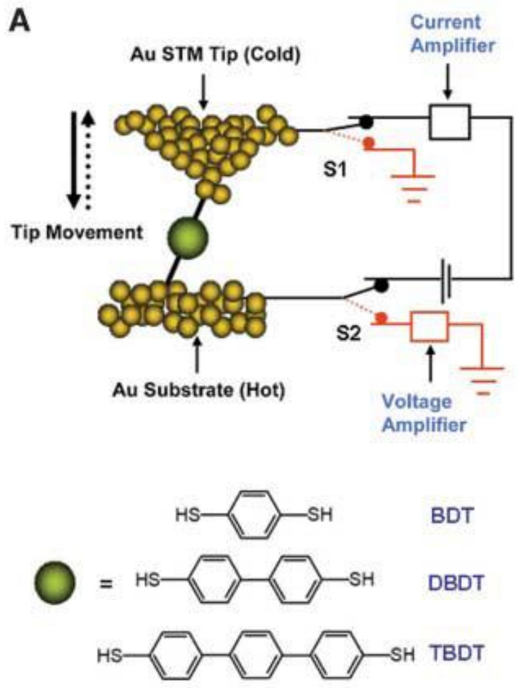




[M. Lee *et. al.*, *Nature Materials* **5** 237 (2006)]




[S. Mukerjee and J. E. Moore, *Appl. Phys. Lett.* **90** 112107 (2007)]

# Thermopower of single molecules



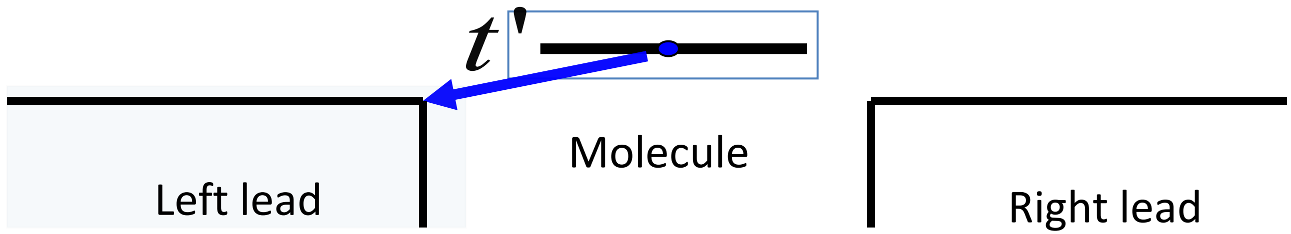

[P. Reddy *et. al.* *Science* **315** 1568 (2007)]

What is the equivalent of small $t$ for molecules?

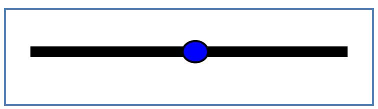
Ans: Weak coupling to leads.

# Molecules

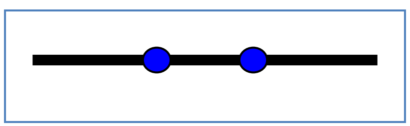
## Anderson model




Ideal leads with hopping $t$ $\quad \Gamma = \frac{2t'^2}{t}$



Energy $\epsilon_d$



Energy $2\epsilon_d + U$

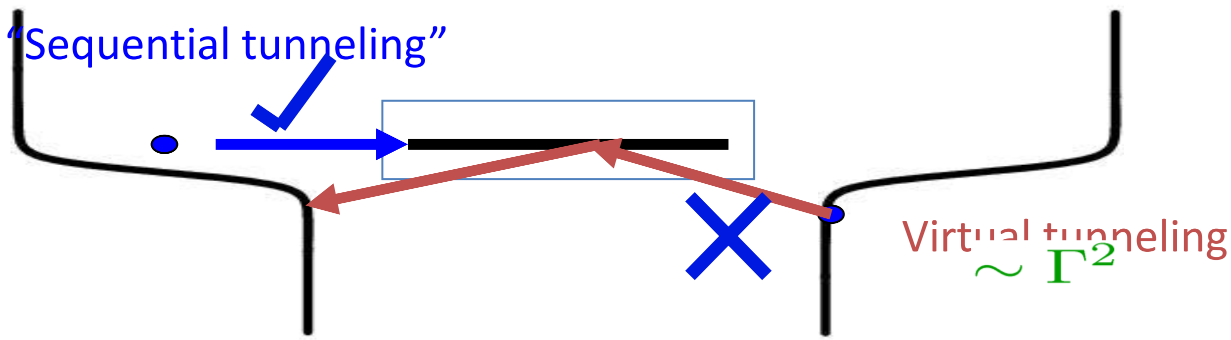
Analytic calculations possible using Landauer formalism for $\Gamma \ll t$ when $U = 0$, and $U \neq 0$ but $\frac{\Gamma}{k_B T} \ll 1$

Violation of Wiedemann-Franz law

Weak coupling limit $\Gamma \ll k_B T$

[P. G. Murphy, S. Mukerjee and J. E. Moore, *Phys. Rev. B* **78** 161406(R) (2008)]

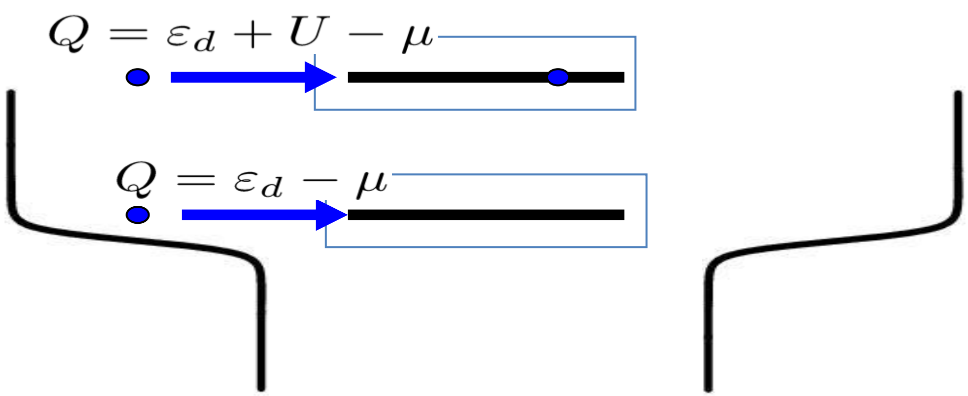
$$\frac{\Gamma}{k_B T} \ll 1$$




$U = 0$

Every electron carries roughly the same amount of heat

Open circuit $\Rightarrow$ # left movers = # right movers $\Rightarrow I_Q \approx 0$



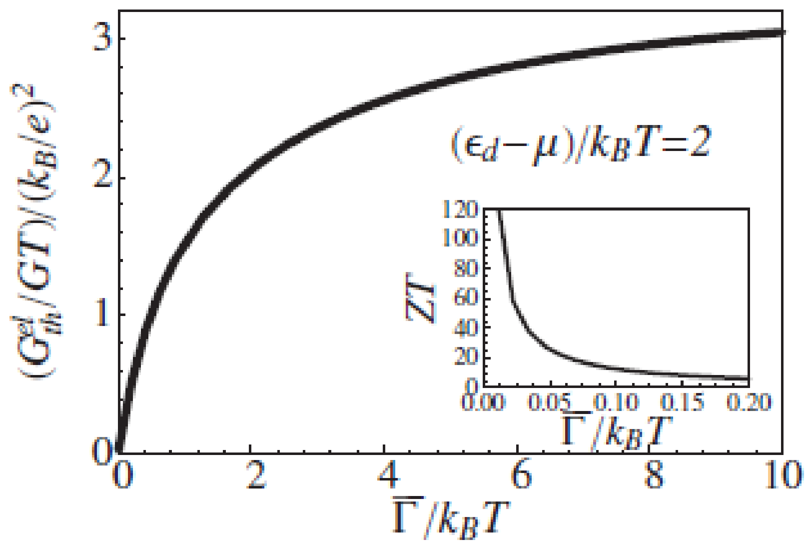

$U > 0$

Open circuit $\Rightarrow I_Q \approx 0$

If $\frac{U}{k_B T} \gg 1$, top level essentially unoccupied and $I_Q \approx 0$

$L_e = \frac{\kappa}{T\sigma} \ll 1$ when $\frac{\Gamma}{k_B T} \ll 1$

## With phonons



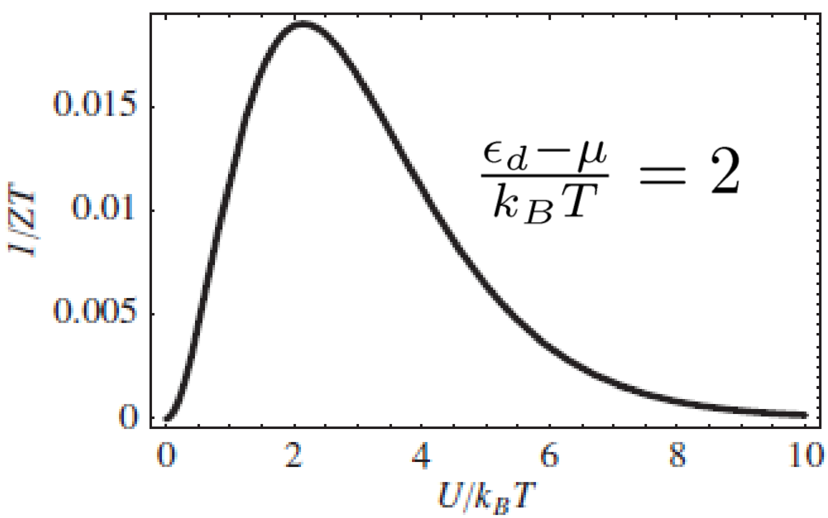

$$G_{ph}^{th} = g_{ph}^{th} \frac{\pi^2}{3} \frac{k_B^2 T}{h}$$

$U = 0$

$$ZT_{max} = \frac{0.51}{\sqrt{g_{ph}^{th}}}$$

at $\frac{\epsilon_d - \mu}{k_B T} = 2.5$

DOS mismatch between phonons in leads and molecule $\Rightarrow g_{ph}^{th} \ll 1$




$U > 0$

$\frac{\Gamma}{k_B T} \ll 1$

$$ZT_{max} = \frac{0.42}{\sqrt{g_{ph}^{th}}}$$

at $\frac{\epsilon_d - \mu}{k_B T} = 2.5$

[P. G. Murphy, S. Mukerjee and J. E. Moore, *Phys. Rev. B* **78** 161406(R) (2008)]

# Summary

1. Analytic calculation possible for $S$ and $L$ and $ZT$ in atomic limit of lattice models with strong correlations.

2. Heikes limit and violation of WF law can be obtained. Consequently electronic limit on $ZT$ cn be very large

3. Requires that the spectral broadening of all conductivities is the same.

4. Why is effective $t$ so low?

# This evening

## Lecture 4: Transport at finite and infinite frequency

- Revisiting the Kubo formula
- Sum rules for conductivities
- Infinite frequency calculation of transport coefficients