Electronic correlations and thermoelectricity
Part II : Seebeck coefficient in correlated metal

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Boltzmann transport (reminder)

- Theory of a gas of particles, with x **and** p
- Quantum aspects of theory are Fermi-Dirac distribution and taking group velocity

$$dN = d^3x d^3p f(x,p)$$

$$p = \hbar k$$

$$f(x,p,t) = f_0(x,p) + \delta f(x,p,t)$$

$$v = \dot{x} = \frac{1}{\hbar}\frac{\partial \epsilon_k}{\partial k}$$

$$\frac{df}{dt} = \frac{\partial f}{\partial x}\dot{x} + \frac{\partial f}{\partial p}\dot{p} + \frac{\partial f}{\partial t} = \mathcal{L}f$$

$$\beta = \frac{1}{k_B T}$$

$$f_0(k) = \frac{1}{\exp\left[\beta(\epsilon_k + \mu) + 1\right]}$$

- Relaxation time approximation

$$\frac{df}{dt} = \mathcal{L}f = -\frac{f - f_0}{\tau}$$

$$j = \sum_k e v_k \delta f_k$$

Conductivity and Seebeck in a Boltzmann theory

- Conductivity

$$\sigma = 2\pi \frac{e^2}{V_0} \sum_k (-\frac{\partial f_0}{\partial \epsilon})|_{\epsilon=\epsilon_k-\epsilon_F} v_k v_k \tau_k$$

band transport function

$$\Phi(\epsilon) = \frac{e^2 2\pi}{V_0} \sum_k v_k^2 \delta(\epsilon - \epsilon_k)$$

$$\sigma = \int (-f_0')\Phi(\epsilon)\tau(\epsilon) d\epsilon$$

- Seebeck coeff.

$$S = -\frac{k_B}{e} \frac{\int (-f_0')\Phi(\epsilon)\tau(\epsilon)\frac{\epsilon-\epsilon_F}{k_B T} d\epsilon}{\int (-f_0')\Phi(\epsilon)\tau(\epsilon) d\epsilon}$$

- Transport integrals

$$L_n = \int d\epsilon (-f_0')\Phi(\epsilon)(\epsilon - \epsilon_F)^n \tau(\epsilon) d\epsilon$$

$$S = -\frac{1}{eT}\frac{L_1}{L_0}$$

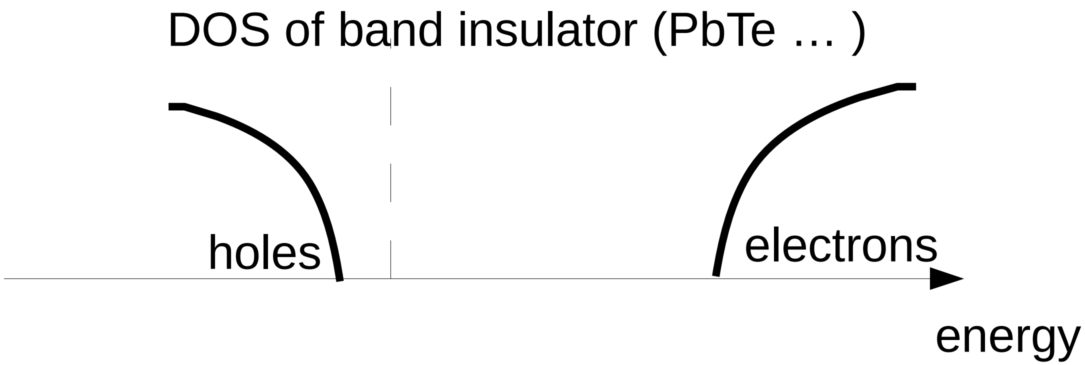
- Seebeck due to particle hole asymmetry in Φ and/or τ

Boltzmann theory of standard thermoelectric materials

- Text book treatment of doped band insulator then evaluates

$$S = -\frac{k_B}{e}\frac{\int(-f_0')\Phi(\epsilon)\tau(\epsilon)\frac{\epsilon-\epsilon_F}{k_BT}d\epsilon}{\int(-f_0')\Phi(\epsilon)\tau(\epsilon)d\epsilon}$$

separating hole and electron contributions, taking



- Most ph asymmetry due to Fermi level close to band edge
- energy dependence of $\tau(\epsilon)$ come from being close to edge,too.
- Temperature dependence encoded in Fermi function

What about systems with strong interactions?

- We have seen in Part I that correlations profoundly modify spectra
- Wave-vector k is not associated to a single frequency component ε_k, so (semi-classical) Boltzmann formulation seems not to be applicable
- What about different T regimes?

Transport in an interacting system

- Kubo formula: expresses response of systems to small perturbations in terms of correlations functions

$$J = -\frac{1}{T} L^{j,j} \nabla \tilde{\mu} + L^{j,j_Q} \nabla(\frac{1}{T})$$

$$J_Q = -\frac{1}{T} L^{j_Q,j} \nabla \tilde{\mu} + L^{j,j} \nabla(\frac{1}{T})$$

$$\tilde{\mu} = \mu + eV$$

$$j_Q = j_E - \mu j$$

$j_E = \sum_k v_k \epsilon_k n_k$ For free el., more complicated in general.

Skipping several parts of derivation. Consult Mahan.

Similarity with Boltzmann expressions

- In large-d (no vertex corrections), one has

$$\sigma = \int \sum_k \left(-\partial f/\partial\omega\right) v_k A_k(\omega) v_k A_k(\omega) d\omega$$

$$S = -\frac{1}{eT}\frac{L_1}{L_0}$$

- Again one can define transport integrals

$$L_n = \int \sum_k \left(-\partial f/\partial\omega\right) v_k A_k(\omega) v_k A_k(\omega) \omega^n d\omega$$

Not being careful about constants here.
Will cancel in S.

- Rewriting with transport function

$$L_n = \int d\omega d\epsilon \Phi(\epsilon) A_\epsilon(\omega) A_\epsilon(\omega) (-\partial f/\partial\omega)\omega^n$$

$$\Phi(\epsilon) = \sum_k v_k v_k \delta(\epsilon - \epsilon_k)$$

$$A_\epsilon(\omega) = -\frac{1}{\pi}\mathrm{Im}\frac{1}{\omega + \mu - \epsilon - \Sigma(\omega)}$$

$$\Gamma_{\mathrm{qp}}(\omega) = -Z\mathrm{Im}\Sigma(\omega)$$

Oudovenko et al. PRB'06

One more integral than in Boltzmann formulation! (states are not poles as a function of energy)

Low T : qp approximation

$$L_n = \int d\omega d\epsilon \Phi(\epsilon) A_\epsilon(\omega) A_\epsilon(\omega) (-\partial f/\partial\omega)\omega^n$$

At low T, however, QP approximation can be made

$$A_\epsilon(\omega) = -\frac{1}{\pi}\mathrm{Im}\frac{Z}{\omega - Z\epsilon + i\Gamma_{\mathrm{qp}}(\omega)} \approx Z\delta(\omega - Z\epsilon)$$

Leading to:

$$L_n = \int d\omega \Phi(\omega/Z)(-\partial f_0/\partial\omega)\omega^n \tau(\omega)$$

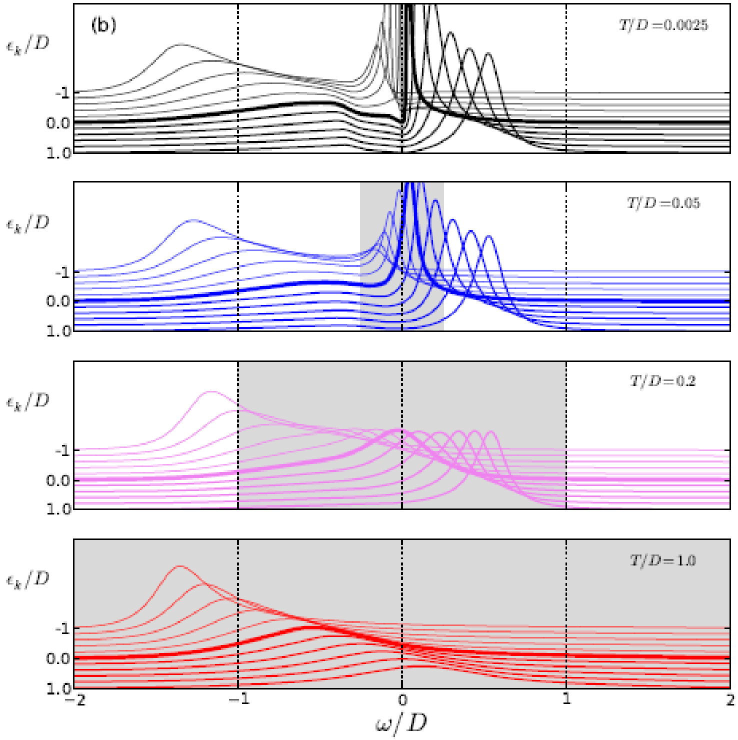
In low T limit, similar form as Boltzmann, but taking transport function at ω/Z, leading to enhancement !

$$S = -\frac{k_B}{eT}\frac{L_1}{L_0} = (1/Z) \times S(\text{for } Z = 1)$$

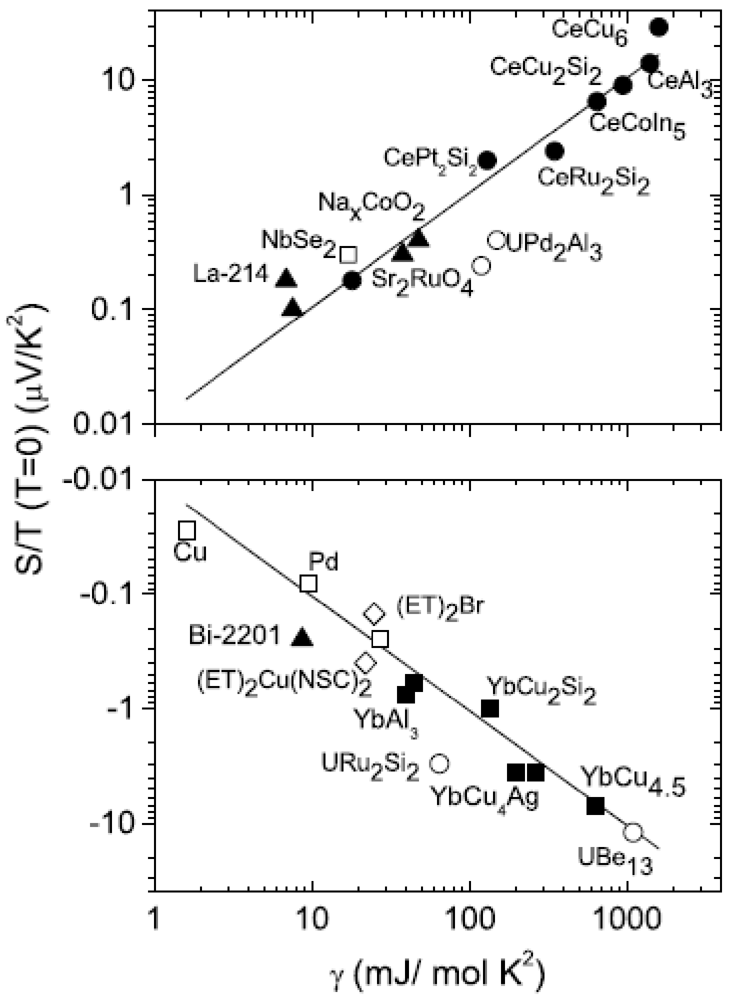
Resillient quasiparticles

- Recent work within DMFT finds dispersing resillient quasiparticle states which validates applicability of Boltzmann-like description even in interacting systems well above Fermi liquid scale

Deng, JM et al. Phys. Rev. Lett. 110, 086401 (2013)
Xu, Haule, Kotliar, Phys.Rev.Lett. 111, 036401 (2013)
Deng et al, arXiv:1404.6480



Low T slope of Seebeck



Scales with 1/Z, like linear coefficient in specific heat.

Behnia, Jaccard, Flouquet
J.Phys CM 2014

Correlations enhance Seebeck!

High-T limit

- As chem. pot ~ T at large T, it is convenient to rewrite

$$j_Q = j_E - \mu j$$

$$\alpha = \Delta V/\Delta T = -\frac{1}{eT}\frac{L^{j,j_Q}}{L^{j,j}} = -\frac{1}{eT}\frac{L^{j,j_E}}{L^{j,j}} + \frac{\mu}{eT}$$

- Assuming energy is bound, the first term vanishes in the high T limit, and Seebeck coefficient is expressed in terms of the thermodynamic values

$$\alpha_{\text{Heikes1}} = \mu/eT,$$

- In metal, Seebeck → 0, at low T is somewhat better behaved

$$\alpha_{\text{Heikes}} = \frac{\mu - \mu(T=0)}{eT}.$$

Evaluating Heikes in atomic limit

From thermodynamic relation (**S** entropy)

$$dE = Td\mathbf{S} - pdV + \mu dN$$

reexpress

$$S_{\text{Heikes}} = \mu/(eT) = -1/e(\partial\mathbf{S}/\partial N)_{E,V}$$

Example 1: single band Hubbard model U $\rightarrow$ 0
spin up and down independent, entropy twice the spin up result

$$\mathbf{S}/k_B = -2\left[(n/2)\log(n/2) + (1-n/2)\log(1-n/2)\right]$$

$$S = -1/e\partial\mathbf{S}/\partial n = -(k_B/e)\log\left[\frac{2-n}{n}\right]$$

Diverges as n $\rightarrow$ 0 and n $\rightarrow$ 2.
Vanishes for particle-hole sym n $\rightarrow$ 1

Chaikin, Beni, PRB'76

Evaluating Heikes in atomic limit

From thermodynamic relation (**S** entropy)

$$dE = Td\mathbf{S} - pdV + \mu dN$$

reexpress

$$S_{\text{Heikes}} = \mu/(eT) = -1/e(\partial\mathbf{S}/\partial N)_{E,V}$$

Example 2: single band Hubbard model U → infinity
for el density n means one has (in atomic limit)

$$\mathbf{S}/k_B = -n\log(n/2) - (1-n)\log(1-n)$$

$$S = -k_B/e\partial\mathbf{S}/\partial n = -k_B/e\log\left[\frac{2(1-n)}{n}\right]$$

Diverges as n → 0 **and** n → 1. Large Seebeck in Mott insulators.

Influence of orbital degeneracies

Doped case with orbital degeneracies d

$$S = -(1/e)\partial \mathbf{S}/\partial n = -k_B/e \log\left[\frac{d_{N+1}(N+1-n)}{d_N(n-N)}\right]$$

Integer filling

$$S = -(1/e)\partial \mathbf{S}/\partial n = \frac{k_B}{2e}\log\left[\frac{d_{N-1}}{d_{N+1}}\right]$$

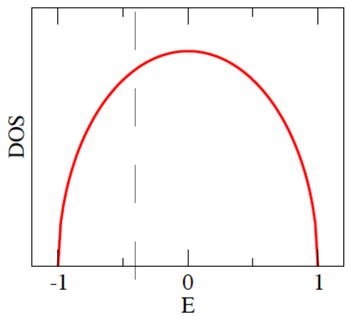
JM and A. Georges, unpublished

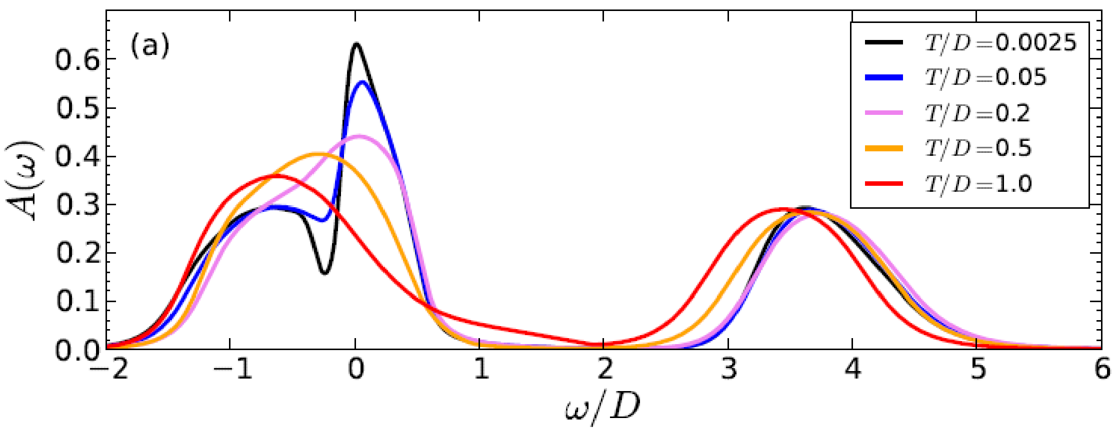
Large ratio between degeneracies increases Seebeck.
Cobaltates $d_6=1$, $d_5=6$. Log 6 additive contribution!

Seebeck coefficient of a doped Mott insulator in DMFT

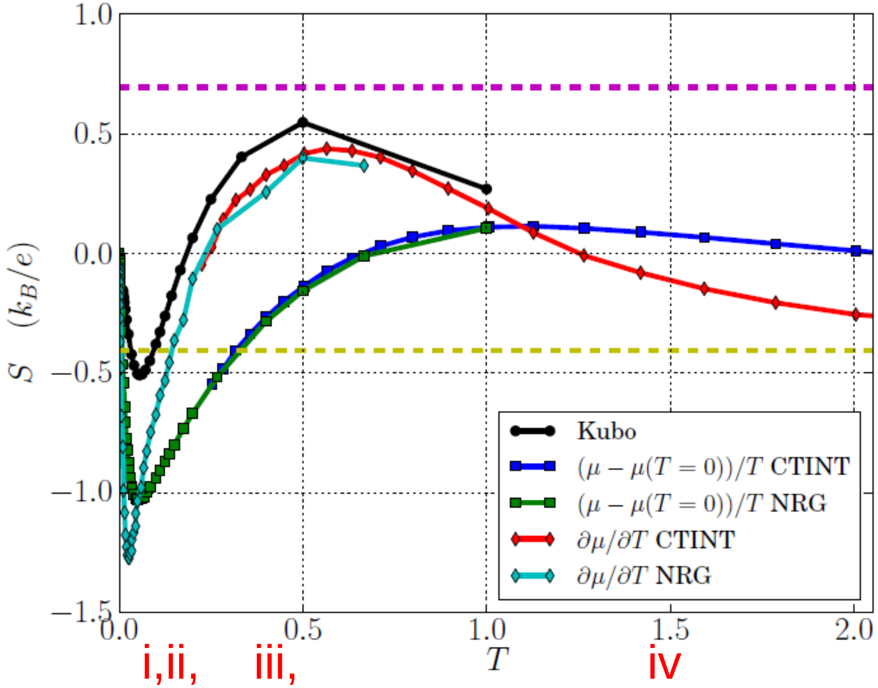
Same simulation as discussed in part I.
Hole-doped Mott insulator in DMFT.
As the DOS temperature is increased, DOS undergoes rich evolution:
- renormalized metal at low T
- atomic like behavior at high T

How is this reflected in Seebeck?



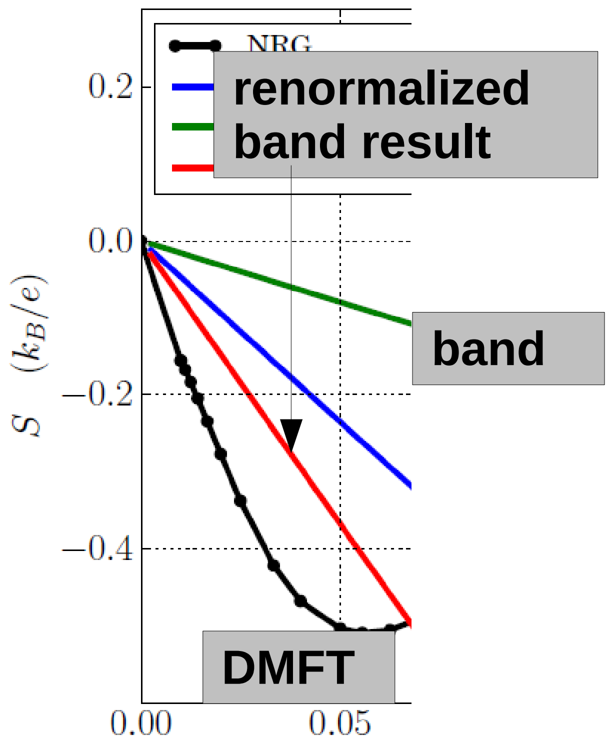


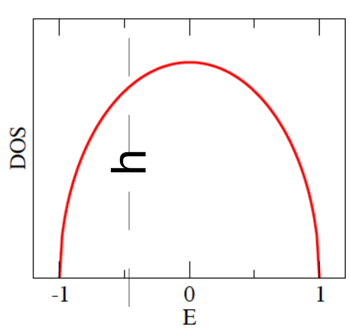
Seebeck coefficient in doped Hubbard model: low T



2 changes of signs.
2 extrema.
4 regimes.
i) FL
ii) Resillient qp
iii)lower Hubbard band
iv) upper Hubbard band

Low-T: renormalized FL with NFL additional corrections





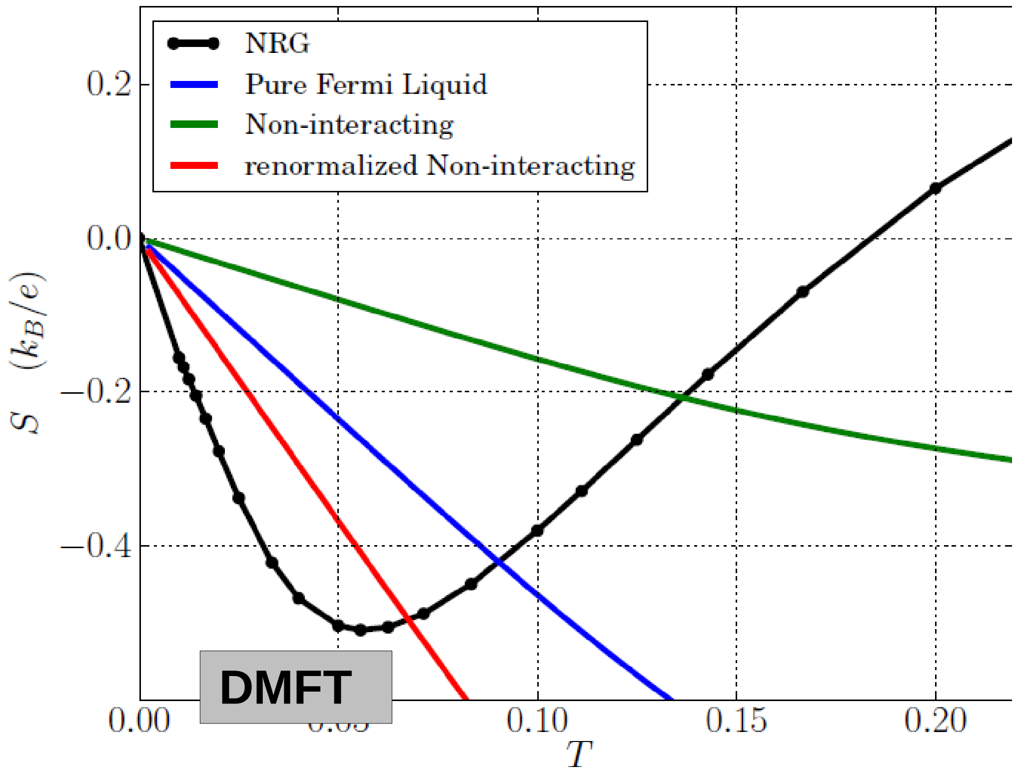
- Linear in T metallic dependence [el-like]
- Low T slope enhanced compared to band result
- Enhancement larger than 1/Z=m*/m (influence of particle-hole asymmetric non-Fermi liquid corrections in scattering rate)

$$\Sigma''(\omega) = \Sigma^{(2)}(\omega) + \Sigma^{(3)}(\omega) + \cdots$$

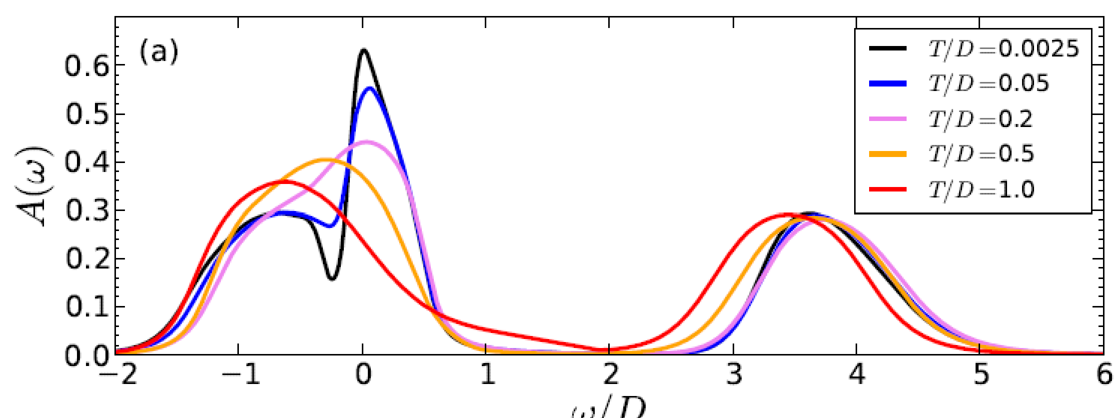
$$\Sigma^{3}(\omega) = \frac{(a_1\omega^3 + a_2\,\omega T^2)}{Z^3}$$

Haule and Kotliar arXiv:0907.0192
Deng, JM et al, PRL'13

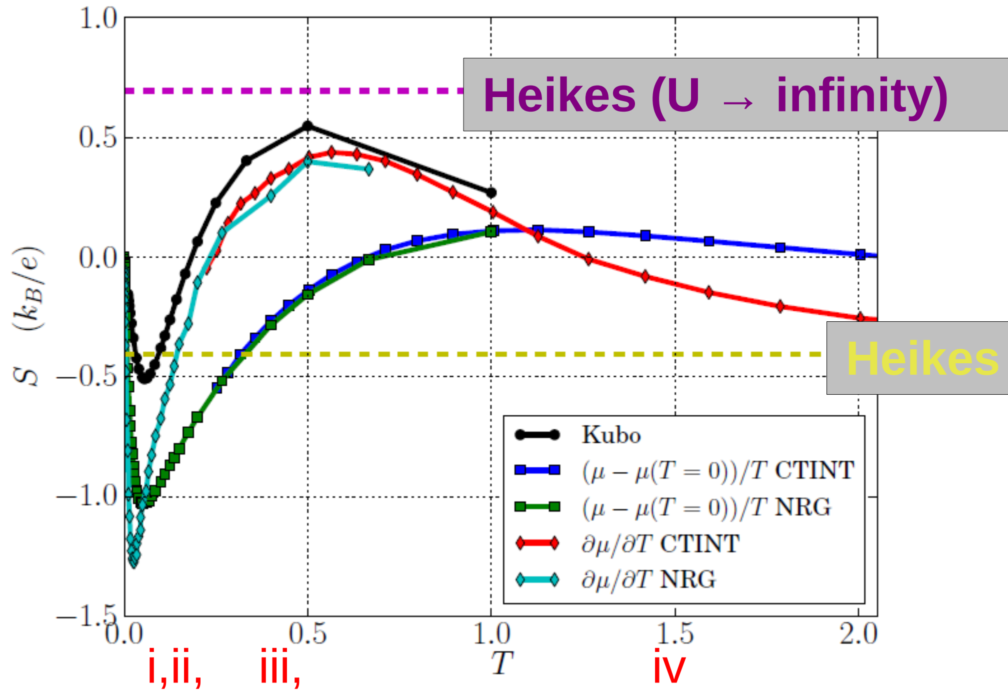
Intermediate T: resillient quasiparticle regime



- Maximum of S
- Progressive but slow decay of resillient quasiparticle excitations



High T 1st and 2nd Heikes regime

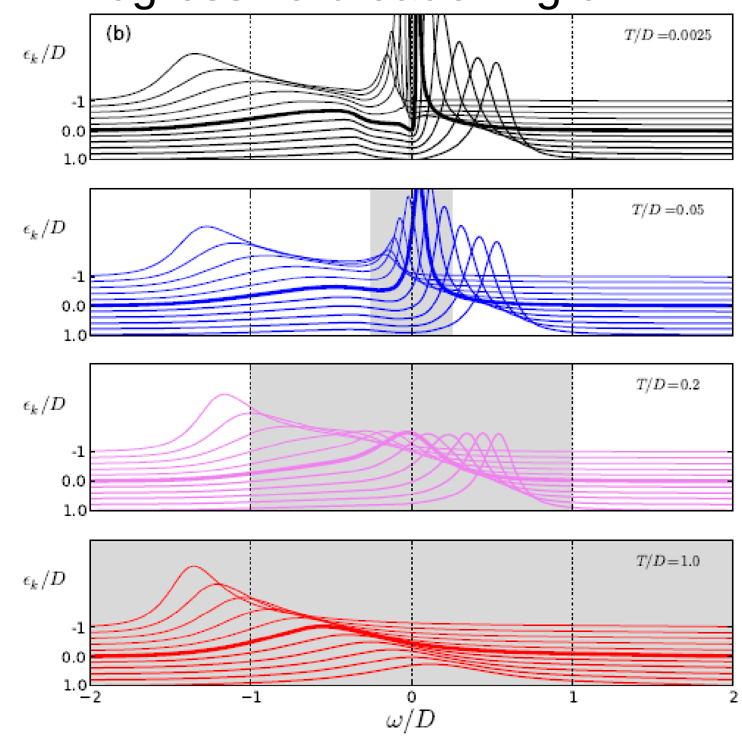


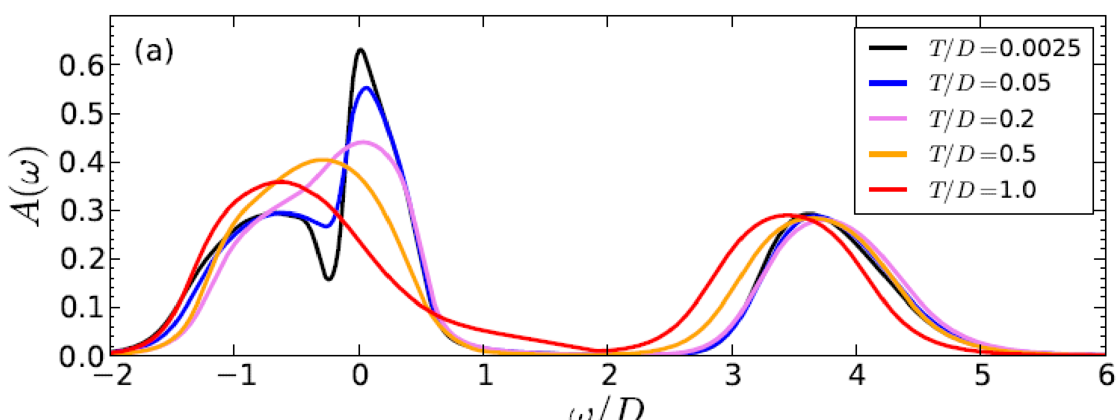
Physics of isolated atom (Hubbard bands).

1st Heikes regime $W_K<T<U$

2nd Heikes regime $T>U$

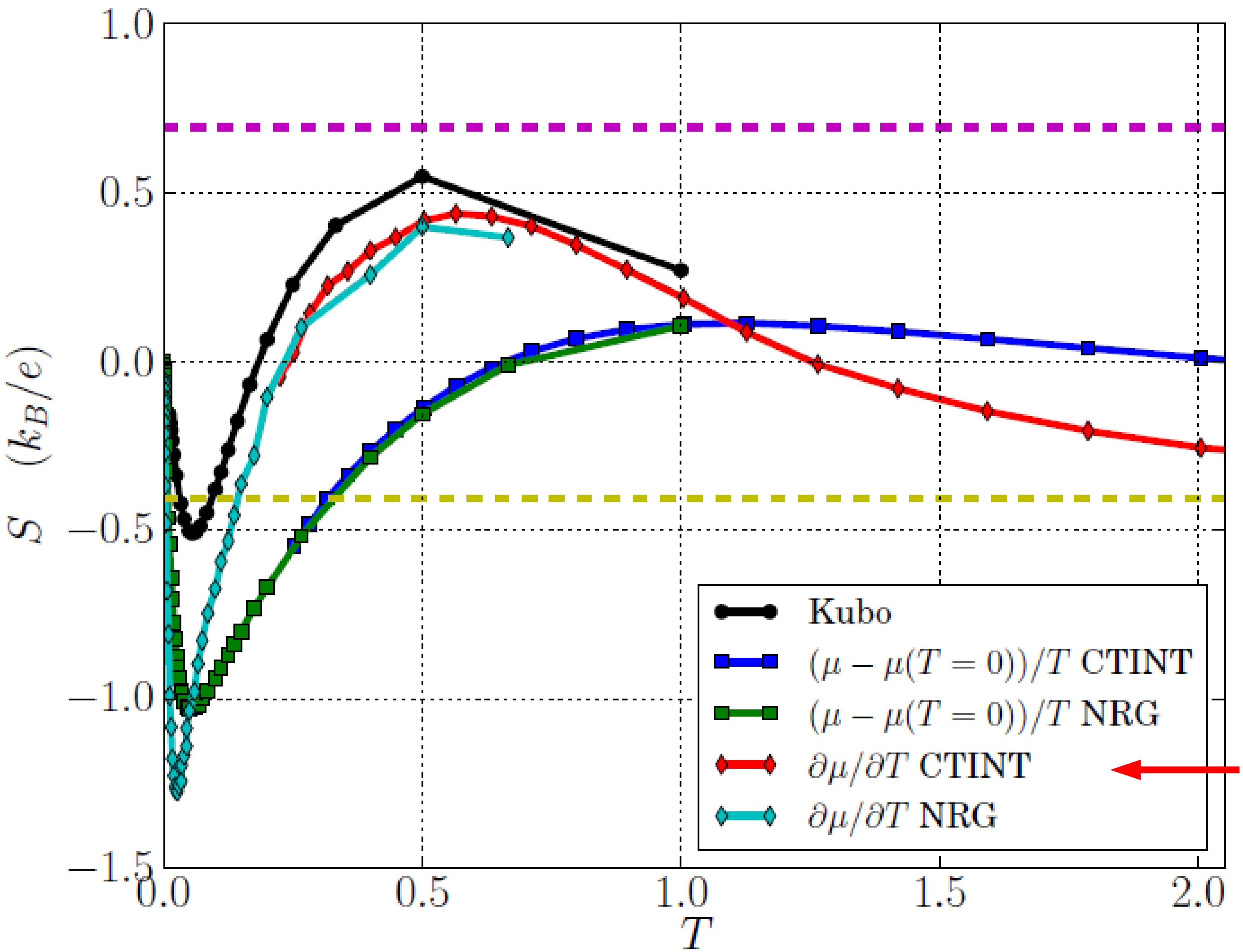
Progressive broadening of T window





High T regime

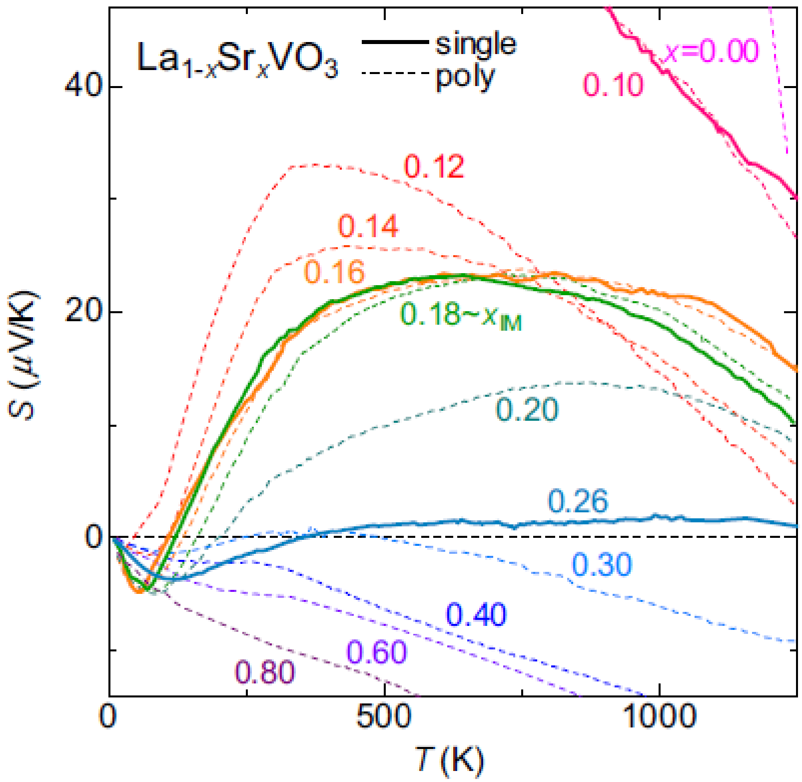
Approaches atomic limits at high T.



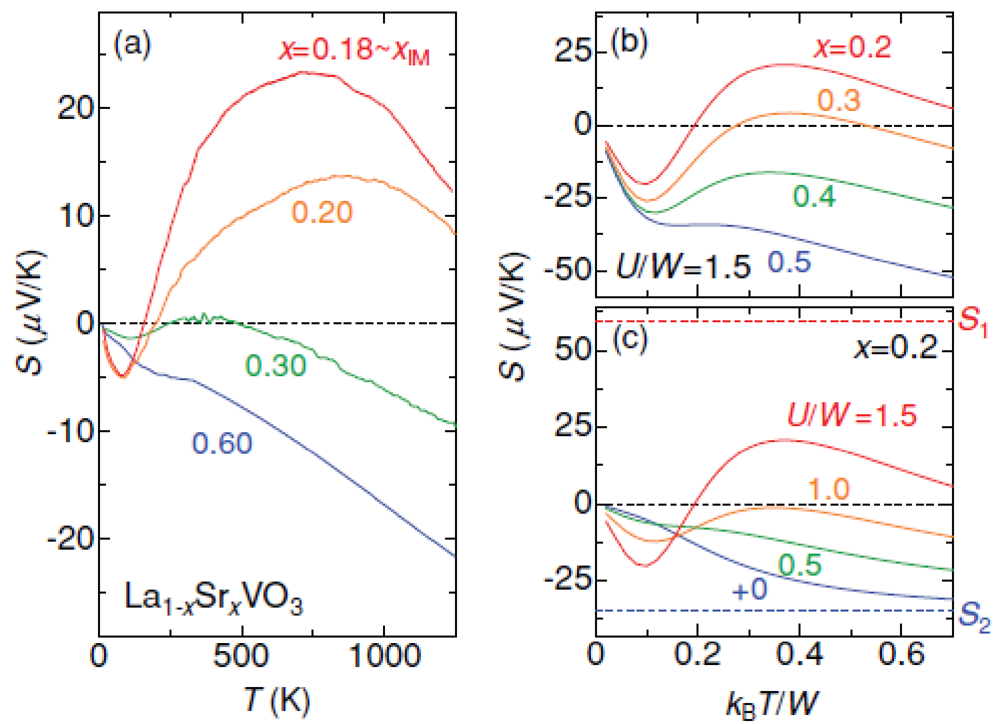
Kelvin formula works
Well.Peterson, Shastry
PRB'2010.

Experiment on doped Mott insulator

- Similar tendencies as theory, several changes of sign, but experimental temperature scale 10 X smaller



Uchida et al. PRB'11



DMFT

- More experiments and applicability of Heikes formla: cf. Sylvie Hebert

Summary

- T-dependent spectral properties manifest also in rich T dependence of Seebeck coeff (changes of sign with T)
- In the low T limit, Kubo formula in quasiparticle approximation equivalent to Boltzmann
- At high T, atomic estimates apply. Entropic content.
- Enhanced Seebeck coefficient at low-T and perhaps also at high-T (potentially, as there is more entropy)

- Not discussed: - successful calculations of thermopower in correlated materials within LDA+DMFT. -figure of merit and challenges associated with optimization
- Perhaps potentially useful even for apliccations, but even if not, understanding of thermopwer important as a probe.

More on entropic content of thermopower

- On board (time permitting)