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

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

$$p = \hbar k$$

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

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

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

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

- 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

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

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

\[ \sigma = \int (-f'_0)\Phi(\epsilon)\tau(\epsilon)d\epsilon \]

- Seebeck coeff.

\[ S = -k_B \frac{\int (-f'_0)\Phi(\epsilon)\tau(\epsilon)\frac{\epsilon-\epsilon_F}{k_B T}d\epsilon}{\int (-f'_0)\Phi(\epsilon)\tau(\epsilon)d\epsilon} \]

\[ S = -\frac{1}{eT} \frac{L_1}{L_0} \]

- Transport integrals

\[ L_n = \int d\epsilon (-f'_0)\Phi(\epsilon)(\epsilon - \epsilon_F)^n \tau(\epsilon)d\epsilon \]

- Seebeck due to particle hole asymmetry in \( \Phi \) and/or \( \tau \)
Boltzmann theory of standard thermoelectric materials

- Text book treatment of doped band insulator then evaluates
  \[ S = -\frac{k_B}{e} \int (-f_0') \Phi(\epsilon) \tau(\epsilon) \frac{e^{-\frac{\epsilon}{k_B T}}}{\int (-f_0') \Phi(\epsilon) \tau(\epsilon) \epsilon} d\epsilon \]
  separating hole and electron contributions, taking

  DOS of band insulator (PbTe … )

- 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 $\varepsilon_k$, 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

\[ J = -\frac{1}{T}L^{j,j} \nabla \tilde{\mu} + L^{j,j\varphi} \nabla \left( \frac{1}{T} \right) \]

\[ J_Q = -\frac{1}{T}L^{j\varphi,j} \nabla \tilde{\mu} + L^{j,j} \nabla \left( \frac{1}{T} \right) \]

\[ \tilde{\mu} = \mu + eV \]

\[ j_Q = j_E - \mu j \]

\[ j_E = \sum_k v_k \epsilon_k n_k \] 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
  \[ \sigma = \int \sum_k (-\partial f / \partial \omega) v_k A_k(\omega) v_k A_k(\omega) d\omega \]

- Again one can define transport integrals
  \[ L_n = \int \sum_k (-\partial f / \partial \omega) v_k A_k(\omega) v_k A_k(\omega) \omega^n d\omega \]

- Rewriting with transport function
  \[ L_n = \int d\omega d\epsilon \Phi(\epsilon) A_\epsilon(\omega) A_\epsilon(\omega) (-\partial f / \partial \omega) \omega^n \]

  \[ \Phi(\epsilon) = \sum_k v_k v_k \delta(\epsilon - \epsilon_k) \]

  \[ A_\epsilon(\omega) = -\frac{1}{\pi} \text{Im} \frac{1}{\omega + \mu - \epsilon - \Sigma(\omega)} \]

  \[ \Gamma_{qp}(\omega) = -Z \text{Im} \Sigma(\omega) \]

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

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

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 \( \omega/Z \), leading to enhancement!

\[ S = -\frac{k_B L_1}{eTL_0} = (1/Z) \times S (\text{for } Z = 1) \]
Resilient quasiparticles

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

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 \( \sim T \) at large T, it is convenient to rewrite

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

\[j_Q = j_E - \mu j\]

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

\[\alpha_{\text{Heikes}} = \frac{\mu}{eT},\]

- In metal, Seebeck \( \rightarrow 0 \), 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)

\[ dE = TdS - pdV + \mu dN \]

reexpress

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

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

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

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

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)

$$dE = TdS - pdV + \mu dN$$

reexpress

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

Example 2: single band Hubbard model $U \to \infty$ for el density $n$ means one has (in atomic limit)

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

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

Diverges as $n \to 0$ and $n \to 1$. Large Seebeck in Mott insulators.
Influence of orbital degeneracies

Doped case with orbital degeneracies $d$

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

Integer filling

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

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: resilient quasiparticle regime

- Maximum of $S$
- Progressive but slow decay of resilient quasiparticle excitations
High T 1\textsuperscript{st} and 2\textsuperscript{nd} Heikes regime

Physics of isolated atom (Hubbard bands).

1\textsuperscript{st} Heikes regime \( W_K < T < U \)
2\textsuperscript{nd} 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
More experiments and applicability of Heikes formula: 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 applications, but even if not, understanding of thermopower important as a probe.
More on entropic content of thermopower

- On board (time permitting)