

Thermopower in Correlated Systems

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Abstract Novel correlated materials discussed recently such as sodium cobaltate Na_xCoO_2 and iron antimonide $FeSb_2$ show considerable promise for attaining high values of thermopower. These extend the limits set by standard semiconducting materials such as bismuth telluride Bi_2Te_3 . Understanding the scale of thermopower and its dependence on material properties is a difficult task, since the Kubo formulas are somewhat opaque. We have developed two alternative approximate formulas that are easier to interpret, while capturing the many body enhancements of thermopower. These are the “high frequency” Seebeck coefficient S^* and the Kelvin formula S_{Kelvin} published recently. This article provides a brief guide to these alternate formulas together with a delineation of their domain of usefulness.

1 Introduction

The aim of this brief chapter is to collect together and introduce the new formulas developed by our group for calculating the Seebeck coefficient for strongly correlated condensed matter systems- along with pointers to some applications. There are two new formulas: the first is the high frequency Seebeck coefficient S^* [1, 5, 6]. It works very well whenever we deal with an effective model that eliminates at the very start, the highest energy scale in the problem. As an example, the t - J model, found by eliminating the large U of the Hubbard model is a good candidate for this formula. Its application to the triangular lattice sodium cobaltate $Na_{.68}CoO_2$

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V. Zlatc and A. Hewson (eds.), *New Materials for Thermoelectric Applications Theory and Experiment*, NATO Science for Peace and Security Series B: Physics and Biophysics, DOI 10.1007/978-94-007-4984-9_2, Springer Science+Business Media Dordrecht 2013

is illustrated in Ref. [2, 3, 4]. The second formula to note is the so called Kelvin formula S_{Kelvin} [5, 6, 7]. Here a modern interpretation of Lord Kelvin's ideas from 1854 leads to a rather useful formula. Its utility is illustrated in applications to the Hubbard model Ref. [9], and also to the interpretation of the "universal change in sign of the Seebeck coefficient in high T_c materials Ref. [8].

In this article, I summarize the various formulas known at present with some comments on their range of validity. I also summarize of the rationale behind the two approximate formulas mentioned above.

2 Comments on the formulae

The formulas are summarized in tabular form below.

- The Kubo formula is a standard and exact result in transport theory, and is eminently useful for non interacting systems. However it becomes hard to apply to most strongly interacting electron systems. In particular retaining vertex corrections becomes difficult and dropping these corresponds to an uncontrolled approximation in general. In systems of current interest, such as Na_xCoO_2 that are describable as doped Mott Hubbard systems, it is difficult to push the analytic evaluation of the Kubo formulas, although for finite size systems (i.e. rather small lattices), it is possible to numerically compute exactly the Seebeck coefficient from this definition [2, 3, 4] and benchmark other approximate formulas against this evaluation.
- The Mott formula is the textbook result of evaluating the Kubo formula for the thermopower of a weakly correlated metal at low temperatures. It expresses this object in terms of the single particle density of states (DOS), the velocity average and the relaxation rate. Being the energy derivative of a logarithm of the product of the three terms, it can be decomposed into *the sum of three types of terms*. This decomposition provides a neat viewpoint, where the thermopower is the sum of the contribution from the energy dependence of the density of states, the Fermi surface average of the velocity square and relaxation time. The weakness of this formula is that it uses the non interacting single particle DOS and does not generalize in any simple way to include interactions.
- The Heikes Mott formula was first noted by Heikes [10] in the context of semiconductors and applied by Mott to the physics of hopping conduction. It corresponds to throwing out the first (and difficult) term of the Kubo formula consisting of a ratio of the current correlations, a justifiable approximation only at very high temperatures. This formula is written in Table.1 with a subtracted $\mu(0)$, to make it well behaved at $T \rightarrow 0$ following Prelovsek et. al. [11]. With this subtraction, the formula even interpolates reasonably between high and low T behaviour- although the low T slope is smaller by a factor of 2 from the answer in the Mott formula DOS contribution [7]. This formula received considerable attention following the work of Chaikin and Beni [12] who applied it to the Hubbard model at essentially infinite temperature. In this limit the sole effect of cor-

relations is to change the entropy in a simple way, and leads to a rough estimate of the scale of the thermopower in Mott Hubbard systems.

- The high frequency Seebeck coefficient S^* was introduced in Ref. [1, 5, 6] in analogy with the earlier work of Shastry, Shraiman and Singh on the Hall constant in correlated materials [13]. The basic idea is that the relaxation time in certain variables- the Hall resistivity, the Seebeck coefficient and the Lorentz number- tends to cancel out, unlike in the corresponding conductivities. Thus at a “high frequency” $\omega \gg \Omega_c$, for an appropriate frequency scale Ω_c , the many body effects are easier to capture in terms of equal time correlation functions of certain fundamental operators. The operators that emerge are related to the sum rules for the relevant conductivities- generalizing in the simplest case- the plasma frequency occurring in the f- sum rule to the corresponding lattice sum rule. They can be computed for various models through a procedure given in Ref. [1, 5, 6]. For models with a restricted Hilbert space, such as the t - J model, this is a very useful formula as shown in Ref [2, 3, 4], and has non trivial predictive power, as we note below.
- The Kelvin formula S_{Kelvin} Ref. [6, 7] honours the contribution of Lord Kelvin [14]. In 1854 Kelvin (then Thomson) used thermodynamical arguments (rather than the then non existent transport theory!) to prove reciprocity between Peltier and Seebeck coefficients. Lars Onsager [15] formulated the correct statement and proof of reciprocity within transport theory much later. In his seminal paper Onsager [15] mentions precursors to his results in the work of Kelvin. It is fascinating to read an account of Kelvin’s reasoning Ref. [14], which boils down to taking the limit of a static perturbation before taking the infinite volume limit. In modern terminology, Kelvin was working in the *slow limit*, whereas transport requires the opposite *fast limit*, where the thermodynamic limit must precede the static limit ¹. Most interestingly Kelvin’s final result of reciprocity shown within the slow limit, survives in the fast limit taken by Onsager!
 After realizing this episode involving two colossi of science, it was natural for the authors to investigate if the slow limit led to interesting approximations. It is remarkable that the final answer of the slow limit [7] is so simple: $S_{Kelvin} = \frac{1}{q_e} \left(\frac{\partial \mathcal{S}}{\partial N} \right)_{T,V}$. It gives substance to the adage that *the thermopower is the entropy per particle*. In Ref. [7, 8, 9] the different formulas are used in the context of different models and benchmarked.
- It is worth mentioning that the availability of different analytical formulas sometimes leads to insights that are not otherwise available. One striking example is the prediction in Ref. [1, 2, 3, 6, 9] of the enhanced Seebeck coefficient in an electronically frustrated lattice- such as the triangular lattice or the FCC lattice. The prediction of a large Seebeck coefficient is for a particular sign of the hopping and was originally motivated by an explicit expression for the high temperature expansion of S^* in Ref. [1] Eqs. (87, 88). In practical terms either the hole doping or the electron doping contains such an enhancement as detailed in

¹ Our discussion of the high frequency S^* above may then be viewed as an *ultrafast limit* where again these variables are well defined.

the above papers. This remains one of the few predictions to come out of theory in this area. Our hope is that the materials community evaluates this prediction experimentally in the near future.

3 Collection of all formulas

Let us note the different formulae in a tabular form:

Table 1: Various Seebeck Coefficient formulae.

Name	Symbol	Formula	Remarks
Kubo	S_{Kubo}	$\frac{1}{T} \frac{\int_0^\infty dt \int_0^\beta d\tau \langle \hat{f}_x^E(t-i\tau) \hat{f}_x(0) \rangle}{\int_0^\infty dt \int_0^\beta d\tau \langle \hat{f}_x(t-i\tau) \hat{f}_x(0) \rangle} - \frac{\mu(T)}{q_e T}$	Exact but hard to implement except in non interacting systems. Here q_e is the charge of the carriers ($- e $ for electrons), \hat{f}_x and \hat{f}_x^E are the charge and energy currents.
Mott	S_{Mott}	$T \frac{\pi^2 k_B^2}{3q_e} \frac{d}{d\mu} \ln [\rho_0(\mu) \langle (v_p^x)^2 \tau(p, \mu) \rangle_{FS}]$	Metals with weak elastic scattering as $T \rightarrow 0$, $\rho_0(\mu)$ is the single particle DOS. Here a momentum average over the Fermi surface is implied, v_p^x the velocity and $\tau(p, \mu)$ the relaxation rate at the chemical potential μ .
Heikes-Mott	S_{H-M}	$(\mu_0 - \mu(T))/q_e T$	Here \mathcal{S} is the entropy and $\mu_0 \equiv \mu(T \rightarrow 0)$. Useful for semiconductors. Note that $\frac{-\mu(T)}{q_e T} = \frac{1}{q_e} \left(\frac{\partial \mathcal{S}}{\partial N} \right)_{E,V}$, and hence differs from the Kelvin formula in the partial derivative variables.
High Frequency Seebeck	S^*	$\frac{\langle \Phi^{xx} \rangle}{T \langle \tau^{xx} \rangle}$	Valid when probe is sufficiently rapid i.e. $\omega \gg \Omega_c$. Here Φ^{xx} and τ^{xx} are the thermoelectric operator and the stress tensor defined in Ref. [1, 5, 6]. Most useful when the model already eliminates high energy states, e.g. in the t - J model Ref. [2, 3, 4] rather than the Hubbard model. Assumes simple relaxation time.
Kelvin	S_{Kelvin}	$\frac{1}{q_e} \left(\frac{\partial \mathcal{S}}{\partial N} \right)_{T,V} = \frac{-1}{q_e} \left(\frac{\partial \mu}{\partial T} \right)_{N,V}$	The two formulas are related by a Maxwell relation. This remarkably simple answer follows from the slow limit. It captures the many body density of states enhancements, while missing velocity and relaxation contributions. Benchmarked in Ref. [7, 9] for the Hubbard model.

4 Acknowledgements

I acknowledge support from DOE-BES Grant No. DE-FG02-06ER46319. Early work was also supported by Grant NSF-DMR 0706128. I am grateful to L. F. Arsenault, A. Garg, J. Haerter, S. Mukherjee, M. Peterson, P. Phillips, A. Shakouri and A. M. S. Tremblay for valuable discussions and collaboration. I thank Veljko Zlatic and Alex Hewson for interesting discussions, comments and encouragement.

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