

Electrothermal transport coefficients at finite frequencies

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Abstract

We review a recently developed formalism for computing thermoelectric coefficients in correlated matter. The usual difficulties of such a calculation are circumvented by a careful generalization of the transport formalism to finite frequencies, from which one can extract the high frequency objects. The technical parallel between the Hall constant and the Seebeck coefficient is explored and used to advantage. For small clusters, exact diagonalization gives the full spectrum for the Hubbard and especially the t - J model, a prototypical model for strong correlations, and this spectrum can be used to compute the exact finite frequency transport coefficients and hence to benchmark various approximations.

An application of this formalism to the physically important case of sodium cobaltate Na_xCoO_2 is made, and interesting predictions for new materials are highlighted.

(Some figures in this article are in colour only in the electronic version)

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Nomenclature

$t(\vec{\eta})$	Hopping matrix element for a distance $\vec{\eta}$	q_e, c	Carrier charge and the velocity of light
$\langle i, j \rangle$	Nearest neighbour sites R_i, R_j	U, J	Interaction coupling constants in the Hubbard and t - J models
$c_{j,\sigma}$	Electron destruction operator at site R_j for spin σ	P_G	Gutzwiller projection operator removing doubly occupied sites
N_s, N, n	Number of sites, electrons and density	$\mu, \rho_0(\mu)$	Chemical potential and density of states per spin at that energy
v, Ω	Volume per cell and total volume	$K = H - \mu \hat{N}$	Grand canonical Hamiltonian
		$C(T), T$	Specific heat and temperature T

$\omega_c = \omega + i0^+$	Frequency with small imaginary part
R_H, R_H^*	Hall constant and high frequency Hall constant
S, L, Z	Seebeck coefficient, Lorentz number and figure of merit
L_{ij}	Onsager response coefficients
M_1, M_2	Response of charge and energy currents to external input power
N_1, N_2	Response of charge and energy densities to external input power
κ, κ_{zc}	The nominal thermal conductivity (L_{22}) and zero current thermal conductivity
E_x, B	Electric and magnetic fields
$\sigma_{\alpha,\beta}$	Electrical conductivity tensor
\hat{J}_x, \hat{J}_x^Q	Charge and heat current operators along x axis
τ^{XX}	Stress tensor or effective mass tensor
Φ^{xx}, Θ^{xx}	Thermoelectric and thermal operators
$\psi(\vec{x}), \phi(\vec{x})$	Luttinger's gravitational field and electric potential
$K(q), \rho(q)$	Heat and charge densities
D_Q, D_c	Heat and charge diffusion constants
$\chi_{A,B}$	Susceptibility of operators A, B
ϵ_n	Energy levels of the Hamiltonian
\vec{S}_j	Spin vector at site R_j

1. Introduction

1.1. The challenge of correlated electron systems

Correlated electron systems [1–7] stand at the frontier of condensed matter physics, posing conceptual as well as calculational hurdles that have seriously engaged the theoretical community in the last few decades. Experimental results on several classes of new materials have provided great impetus to this study, and often given direction to the theoretical endeavours. High T_c superconductors are a large class of materials that are within the domain of correlated electron systems, but are not the only ones. The study of rare earth compounds provides another important class of systems, as do the newly discovered cobalt oxide materials.

Correlated electron systems are characterized by a common feature, namely a narrow bandwidth of electrons, which interact strongly on a scale of the order of electron volts at short distances. The dimensionless coupling constant, namely the ratio of the interaction energy U (\sim a few electronvolts) to the band width W (\sim 0.1 or 1 eV), becomes large. This large parameter makes the validity of a perturbation theory in U/W unclear. In weakly interacting systems, such as good metals, the analogous ratio is small and leads to the Fermi liquid picture of weakly interacting quasiparticles, as formulated by Landau and others. In the case of correlated matter, as in many other settings, the behaviour of perturbation theory has a strong dependence on spatial dimensionality. In one dimension, the standard Fermi liquid theory breaks down due to a proliferation of low energy excitations, i.e. an infrared breakdown. The most interesting case of two dimensions, i.e. electrons moving in a plane, is the hardest problem yet, since

special techniques that work in 1D are not applicable here, and yet the low dimensionality suggests enhanced quantum fluctuations. This case is of experimental consequence, since many correlated materials are also layered, displaying a large asymmetry between their transport properties along planes and across these planes.

The basic models that have been used to describe correlated electrons are the Hubbard and t - J models described below and the periodic Anderson and Kondo lattice models. More complex models with multiple bands have been considered, but in this paper we shall restrict our attention to the first two models, which describe a very large class of systems where d-type electrons are involved. In physical terms the Hubbard model $H = H_0 + H_1$ contains the hopping of electrons between sites denoted as $H_0 = -\sum_{\vec{\eta}, \vec{x}} t(\vec{\eta}) c_{\vec{x}+\vec{\eta}, \sigma}^\dagger c_{\vec{x}, \sigma}$, where $t(\vec{\eta})$ is the hopping matrix element for a range vector $\vec{\eta}$,¹ and on-site Coulomb repulsion terms $H_1 = U \sum n_{j\uparrow} n_{j\downarrow}$. This model neglects all other (smaller) terms in the full lattice Coulomb problem. It is thus the simplest correlated electron model, characterized by the dimensionless coupling $U/|t|$ and the filling of electrons in the band denoted by $n = N/N_s$ (where N and N_s are the total number of electrons and the number of lattice sites), so that from the Pauli principle we are restricted to the range $0 \leq n \leq 2$. The so-called ‘Mott–Hubbard gap’ arises in this model at half filling $n = 1$ as follows. At this filling, there is a single electron per site on average, and so it is impossible to avoid paying an energy penalty of $O(U)$ on adding a particle, but it is quite cheap (independent of U) to remove a particle. Thus the cost of adding a particle is quite different from removing a particle. This fundamental asymmetry characterizes an insulating state in the most general possible terms. It does not invoke any kind of broken symmetry whatsoever. Such an insulator is called the Mott–Hubbard insulator. The standard example of this kind of insulator is the 1D Hubbard model at half filling.

Another important description of correlated electron systems is through the t - J model. This model represents a much stronger version of correlations, with the prohibition of double occupancy, i.e. states with $n_{j\uparrow} n_{j\downarrow} = 1$. This constraint is enforced by the Gutzwiller projection operator

$$P_G = \prod_j (1 - n_{j\uparrow} n_{j\downarrow}), \quad (1)$$

so that $H_{t-J} = P_G T P_G + \text{exchange}$. This situation corresponds to taking $U \rightarrow \infty$ in the Hubbard model. The added exchange term is written as $J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j$ and represents the tendency, arising from eliminating high energy states with double occupancy, of neighbouring spins to point in antiparallel directions².

Given these simple looking models, the task is to compute physically measurable variables, such as the thermodynamic response functions as well as the dynamical response functions.

¹ The band width on simple lattices is related to the hopping through $W \sim 2\nu|t|$ where ν is the coordination number of the lattice. The vector $\vec{\eta}$ is usually, but not always, specialized to be the set of nearest neighbour vectors on the lattice.

² By performing degenerate perturbation theory at large U one can obtain the t - J model and another small three body term that is neglected here [8].

One wants to understand the nature of the order in the ground states that arise and the dependence of these on various parameters of the models. Various calculations suggest highly non-trivial magnetic and superconducting states to emerge from these simple models. Among the dynamical aspects of the problems, transport variables such as resistivity form the bulk of measurements carried out in laboratories; these are the table top experiments of condensed matter physics. Here one applies an electrical and a thermal gradient along the sample (say along the x axis) and in some instances a uniform magnetic field transverse to the electric field (along the z axis). The measured objects are the electrical and thermal currents that are induced, and by taking the ratio of currents to fields, one deduces the various conductivities $\sigma_{\alpha,\beta} = \partial J_{\alpha} / \partial E_{\beta}$ and from these the resistivities (see equations (3), (13) and (14) below). They are relatively easy to measure, and reveal the characteristics of a given material to a very large extent, e.g. whether it is a metal or an insulator, the carrier charge and density, etc. Next to resistivity, one of the most widely used measurements is that of the Hall constant R_H (defined below in equation (3)), followed by the thermoelectric response functions such as the thermal conductivity κ (defined below in equation (17)), the Seebeck coefficient S and the Lorentz number L (defined below in equation (68)). The materials community has also great interest in seeking the conditions for an enhanced Seebeck coefficient and the figure of merit ZT equation (68), since the overall efficiency of a device turns out to depend upon this dimensionless number.

Unfortunately it is not a simple matter to compute these response functions. In particular, these are much harder than equal time correlations. One needs to know more than the ground state in order to determine these, a handle on the excitations is also required. Thus the question of *transport in correlated matter* is one of the hardest problems in condensed matter physics. The traditional methods and models of transport such as Drude–Sommerfeld [9, 10] and Bloch–Boltzmann [11, 12] theories have been used extensively to estimate answers, even when the validity of the methods is rather ambiguous in these systems. The simplest of these is the Drude–Sommerfeld model [9], using a free electron gas within a Boltzmann equation approach, and thereby builds in the Fermi statistics into the classical Drude theory. The Bloch–Boltzmann [11–13] theory improves on this by focusing on carriers in the Bloch bands, and thus the carriers are characterized by a band index as well as a wave-vector index and relies principally on the concept of metals and insulators as defined by band filling. This band filling concept is often denoted as the Bloch–Wilson [12, 13] classification of metals and insulators. Landau theory of Fermi liquids [14] further refines the theory and incorporates the effect of Coulomb interactions via renormalized quasiparticles. Thus the physical picture behind the current understanding of transport is one of almost free quasiparticles that diffuse through matter, suffering multiple collisions either mutually or with the lattice and other excitations.

The above picture is not robust against strong correlations. Mott–Hubbard interactions change the nature of the carriers radically near half filling, i.e. a single electron per atom. The

Mott insulating state [15] arises as an exception to the Bloch–Wilson [12, 13] classification of metals and insulators. At half filling a Mott–Hubbard system *is an insulator due to correlations* and would have been a metal without interactions. The strongly correlated systems addressed in this paper may be described as doped Mott insulators [6], i.e. states obtained by adding or removing electrons from a Mott insulator. Here the definition of a quasiparticle has been argued to be ambiguous [6, 16], thus making the standard approach questionable. The applicability of the Fermi liquid concept has been questioned in strongly correlated matter, on the basis of several experimentally anomalous results for resistivity and photoemission [7, 17].

In this review, we address this question from a fresh point of view, starting from the exact but usually intractable linear response formulae, generally known as Kubo formulae, and finding easier but non-trivial versions of these. These new formulae approximate certain aspects of the problem that are possibly less controversial, but treat the effects of correlations carefully. Our results may be classified as being complementary to the usual Bloch–Boltzmann theory, and we present the formalism as well as its applications in the context of the thermoelectric response functions. In short, our method enables us to compute a well-defined subset of the transport response functions, such as the Seebeck coefficient, the Hall constant and the Lorentz number as well as the thermoelectric figure of merit. This subset, described in greater detail below, is characterized by the fact that they are independent of the relaxation times, within the simplest Bloch–Boltzmann theory.

1.2. Transport in correlated electron systems

As explained above, a major problem is to understand transport phenomena in correlated matter. Traditional approaches such as the Boltzmann equation have served long and distinguished tenures to explain transport coefficients in terms of a few measurable objects (relaxation times, effective masses, etc). However, these methods run into severe problems in the most interesting and important problem of metals, with strong Mott–Hubbard correlations. These correlations give a Mott insulating state at commensurate (half) filling, with localized spins interacting with each other, and away from half filling, one has metallic states that carry the distinguishing marks and signatures of the parent Mott insulator.

The high T_c systems provide one outstanding set of materials that have dominated the community for the last 20 years. These are widely believed to be strongly correlated, following Anderson’s original and early identification of these as doped Mott insulators [16]. Another important material, sodium cobaltate Na_xCoO_2 , has recently been popular in studies of thermoelectricity [18, 19]; this is strongly correlated too, but the underlying lattice is triangular rather than square. These two systems have in common the presence of spin half entities, and have both been modelled in the (rather extensive) literature by some variants of the t – J model.

The qualitative reason for the difficulties of the Bloch–Boltzmann equation approach in these correlated models can be understood in several ways. One is to recognize from a

variety of experiments in these systems that the wave function renormalization or quasiparticle residue z_k (defined as the jump in the ground state occupation number at the Fermi surface in momentum space) is either zero or if non-zero, it is certainly very small. Another simple and yet powerful point of view is to ask: what is the charge carrier in a Mott–Hubbard system near half filling? From the real space point of view, in order that a correlated electron can hop to a nearby position, it must make sure that there is no particle of either spin at that site. This is unlike the situation for an uncorrelated electron, which can always hop, regardless of the opposite spin occupancy of the target site. Hence the motion of a correlated electron of either spin is accompanied by the ‘backflow’ of a vacancy. It is therefore clear that the carriers are best viewed as holes *measured from half filling*. Thus at a filling of electrons $n \equiv N/N_s$ (where N and N_s are the total number of electrons and the number of lattice sites), the carriers are in fact $\delta = |1 - n|$, so that near half filling $\delta \rightarrow 0$, and one sees that the carriers are frozen out. Thus the overall scale of several transport coefficients can be found almost by inspection; for example, the Hall number must vanish as we approach half filling, as must the inverse thermopower, defined below in equation (15). However, it is already clear that the Bloch–Boltzmann approach cannot easily capture these ‘obvious results’. The latter starts with the band structure derived quasiparticles, and as $n \rightarrow 1$ has no knowledge of the impending disaster, also known as the Mott insulating state! One can also view this issue from the point of view of real space versus momentum space definition of holes: the correlated matter clearly requires a real space picture to make physical sense (as opposed to computational ease), whereas the Bloch–Boltzmann approach takes a purely momentum space approach to particle and holes. In fact, the ‘Bloch–Boltzmann holes’ are vacancies in momentum space measured from a *completely filled band* and have no resemblance to the Mott–Hubbard holes. Of course, the above diatribe obscures a crucial point; the Mott–Hubbard real space holes viewpoint is almost impossible to compute with, at least using techniques that exist so far. On the other hand, the momentum space view is seductive because of the ease of computations exploiting a well-oiled machine, namely, the perturbative many body framework. Hence it seems profitable to explore methods and techniques that implement the Mott–Hubbard correlations at the outset and give qualitatively correct answers. Our formalism, described below, was motivated by these considerations.

In this review, there will be little effort at an exhaustive literature survey. However, it is appropriate to mention that the problems discussed here have been addressed by several authors recently. Mahan’s papers [20] address issues in low carrier density thermoelectric materials, including superlattices. Dynamical mean field theory, reviewed in [21], has been applied to the problem of thermoelectricity in [22]. A considerable body of theoretical and experimental work on heavy Fermi systems and relevant models can be found in the work [23]. In particular, the review paper [24] summarizes the work on the Falicov–Kimball model as an application of the dynamical mean field theory.

Our published papers contain more references to other approaches taken in the literature. I would, however, like to mention that at a ‘mean field theory’ level, the Mott–Hubbard correlations *can be built in*, by various slave Boson or slave Fermion approaches, with some success [6]. In essence, strong correlations force us to deal with the Gutzwiller projection in equation (1) of the Fermi operators

$$\hat{c}_{j\sigma} = P_G \hat{c}_{j\sigma} P_G, \quad (2)$$

and a similar expression for the creation operators. The sandwich of the operators by P_G makes sure that the states considered have no double occupancy; P_G annihilates those states. However, the operators $\hat{c}_{j\sigma}$ are no longer canonical Fermions, i.e. do not satisfy the usual anticommutation relations. One finds that $\{\hat{c}_{j\sigma}, \hat{c}_{l\sigma}^\dagger\} \neq \delta_{j,l}$, but rather a non-trivial term appears on the right-hand side. One way to avoid dealing with the $\hat{c}_{j\sigma}$ operators is to represent the effects of the Gutzwiller projection, using auxiliary (‘slave’) Fermi or Bose operators to force the constraint of no double occupancy [6]. These slave fields consist of canonical Fermions or Bosons, but with an added constraint at each site and in order to deal with that constraint end up making Hartree type factorization of resulting expressions. The errors made by these factorizations are hard to quantify, but do give some qualitative understanding of transport in many cases.

Since well-controlled calculations are difficult to perform for the experimentally relevant case of two dimensions with electrons having spin $\frac{1}{2}$, we are most often forced into numerical computations. The formalism developed here provides some guidance towards effective computations. We expect that our formalism is to be supplemented by a heavy dose of numerics, either exact diagonalization or some other means.

1.3. Plan of the article

In section 2, we motivate the high frequency approach through the example of the Hall constant. For the triangular lattice sodium cobaltate, this leads to the interesting prediction of a T linear Hall constant, which has been verified experimentally. In section 3 we obtain the finite frequency thermoelectric response functions, by using a dynamical version of Luttinger’s gravitational field as a proxy for the thermal gradients. From this formalism, novel sum rules for the thermal conductivity and new thermal and thermoelectric operators emerge. We obtain useful formulae for the variables of common interest such as the Seebeck coefficient and the figure of merit. In section 4 we present the result of applying these formulae numerically to sodium cobaltate and benchmark the high frequency approximation by comparing with the exact evaluation of Kubo’s formulae. We show how our formalism gives a quantitatively accurate result for existing materials. It further leads to interesting and possibly important predictions for the Seebeck coefficient of as yet undiscovered materials. In section 5 we present a simple diffusion relaxation model for coupled charge and heat currents in metals, where the new operators play an explicit role, and their meaning is made physically clear. The model and some novel response functions relating to an applied ac power source are likely to be of interest in the context of pulsed laser heating in materials.

2. Hall constant

The basic idea of this approach is well illustrated by the example of the Hall constant for correlated matter R_H defined in equation (3). Here the initial paper of Shastry, Shraiman and Singh [25] pointed out that the *dynamical Hall constant* is better suited for computation in correlated systems. Consider the simplest framework, the Drude theory of electrons [9, 26], where we know that

$$\begin{aligned}\sigma_{xx}(\omega) &= \frac{\sigma_{xx}(0)}{(1 + i\omega\tau)}, \\ \sigma_{xy}(\omega) &= \frac{\sigma_{xy}(0)}{(1 + i\omega\tau)^2},\end{aligned}\quad (3)$$

$$B R_H \equiv \rho_{xy}(\omega) = \frac{\sigma_{xy}(\omega)}{\sigma_{xx}(\omega)\sigma_{yy}(\omega)} = \frac{B}{nq_e c},$$

where $q_e = -|e|$ is the electron charge, n the density of electrons, τ the relaxation time and B the uniform magnetic field along the z axis. The relaxation time cancels out in computing the Hall resistivity at arbitrary frequencies, and this cancellation gives us a clue. We might as well compute the two conductivities $\sigma_{\alpha\beta}(\omega)$ at *high frequencies*, since here the notorious difficulties inherent in computing the dc values of these objects vanish. The Drude theory therefore gives us an important insight, namely, that the *Hall resistivity* is less ω dependent than the *Hall conductivity*. We explore and build on this central idea further in this paper, using exact diagonalization, dispersion relations and sum rules.

In order to perform the above suggested calculation, we need to take the Kubo formulae for the conductivities³ and take the appropriate ratios to get the dynamical resistivity. Let us consider the electrical conductivity $\sigma_{\alpha\beta}(\omega)$ of a general Fermionic system defined on a lattice. Let us define an energy dispersion ε_k obtained by Fourier transforming the hopping matrix element $t(\vec{\eta})$ as $\varepsilon_k = -\sum_{\vec{\eta}} \exp -i\vec{k} \cdot \vec{\eta} t(\vec{\eta})$. The electrical current operator is obtained using the continuity equation as

$$\vec{J} = i q_e \sum_{\vec{x}, \vec{\eta}} t(\vec{\eta}) \vec{\eta} c_{\vec{x}+\vec{\eta}, \sigma}^\dagger c_{\vec{x}, \sigma}. \quad (4)$$

The current operator \hat{J}_α is dressed by a suitable Peierls [28] phase factor in the presence of the uniform magnetic field B along the z axis. In the t - J model, the current is sandwiched by the Gutzwiller projector in equation (1) as $\hat{J} \rightarrow P_G \hat{J} P_G$, and thereby allows transport only between singly occupied sites. We can use perturbation theory to linear order in the external electric field to find a general expression for the dynamical conductivity [10, 25]:

$$\begin{aligned}\sigma_{\alpha\beta}(\omega_c) &= \frac{i}{\hbar N_s v \omega_c} \left[\langle \tau^{\alpha\beta} \rangle + \hbar \sum_{n,m} \frac{p_n - p_m}{\varepsilon_n - \varepsilon_m + \hbar\omega_c} \right. \\ &\quad \left. \times \langle n | \hat{J}_\alpha | m \rangle \langle m | \hat{J}_\beta | n \rangle \right],\end{aligned}\quad (5)$$

³ It is frustrating that despite several ambitious claims in the literature, especially from the Mori formulation experts, there is no practical and direct way of computing the dynamical *resistivity* that bypasses the intermediate stage of computing the dynamical *conductivities* [27].

where $p_n \propto e^{-\beta\varepsilon_n}$ is the probability of the state n , and the ‘stress tensor’ (sometimes called the ‘effective mass tensor’) is defined by

$$\tau^{\alpha\beta} = q_e^2 \sum_{k,\sigma} \frac{d^2\varepsilon(k)}{dk_\alpha dk_\beta} c_\sigma^\dagger(k) c_\sigma(k), \quad (6)$$

where v is the atomic volume and $\omega_c = \omega + i0^+$. The Hall conductivity, in fact, involves the antisymmetric part of this tensor [25]. In the case of a t - J model the τ operators are also sandwiched by Gutzwiller projection in equation (1). In order to compute say the transport conductivity $\Re \sigma_{xx}(\omega)$ in the limit $\omega \rightarrow 0$, we need to sum over terms such as $\sum_{n,m} p_n \delta(\varepsilon_n - \varepsilon_m) \langle n | \hat{J}_\alpha | m \rangle \langle m | \hat{J}_\beta | n \rangle$. Such a computation is made very difficult by the presence of the Dirac delta functions. These energy conserving delta functions lead to a finite limit for $\sigma^{xx}(0)$ in say a disordered metal. The limit is reached only in the thermodynamic limit by a subtle limiting process and corresponds to a dissipative resistivity. These delta functions are very hard to deal with, if we are given a set of energy levels for a finite system. It is then necessary to broaden the delta functions to a suitable function, say a Lorentzian with an appropriate width determined by the system size and other parameters. In practice, this task is quite formidable and only rarely has it been undertaken, thereby motivating the search for alternative routes.

Following the hint contained in the Drude formulae, we can take the high frequency limits for the conductivity and thereby obtain the Hall resistivity at high frequencies

$$R_H^* \equiv \lim_{\omega \rightarrow \infty} R_H(\omega) = \frac{-i N_s v \langle [\hat{J}_x, \hat{J}_y] \rangle}{B \hbar \langle \tau^{xx} \rangle^2}. \quad (7)$$

In deriving this formula, one is working in the non-dissipative (reactive) regime. That is because the Kubo formulae in equation (5) are evaluated away from the $\omega \rightarrow 0$ limit, where the Dirac delta functions come into play.

The main article of faith is the claim that $\rho_{xy}(\omega)$ at large frequencies is related in a simple way to the transport variable $\rho_{xy}(0)$. Is this rationalizable? Further, what is the meaning of high frequency or how ‘high’ is ‘high enough’?

With regard to the magnitude of the frequency, the key point is to work with a projected Fermi system rather than a bare one. For example, in the case of the Hubbard model versus the t - J model, one sees that the energy scale inequality requirement is

$$\hbar\omega \gg \{|t|, U\}_{\max}, \quad (8)$$

$$\hbar\omega \gg \{|t|, J\}_{\max}. \quad (9)$$

Thus in the case of the t - J model, one can be in the high frequency limit, and yet have a modest value of ω , in contrast to the Hubbard model since usually U is large, $O(ev's)$. In the case of the cobaltates, the energy scale that determines the high frequency limit is presumably the Hunds rule or crystal field energy and hence much lower. Thus the ‘high frequency limit’ is expected to be close to the transport values, for models where the high energy scale is projected out to give an effective low energy Hamiltonian with suitably projected operators.

Subsequent studies show that this simple formula (equation (7)) is a particularly useful one; we list some of

its merits:

1. It is exact in the limit of simple dynamics, as in the Bloch–Boltzmann equation approach.
2. It can be computed in various ways, e.g. using exact diagonalization [29] and high T expansions [25, 30].
3. We have successfully removed the dissipational aspect of the Hall constant here and retained the (lower Hubbard sub-band physics) correlations aspect. This is done by going to high frequencies and using the Gutzwiller projected Fermi operators in defining the currents.
4. It is valid for the entire range of hopping processes, from hopping type incoherent transport at high T to coherent Fermi liquid type transport at low T in a band system.

We emphasize that this provides a very good description of the t – J model, where this asymptotic formula requires ω to be larger than J , but should not be expected to be particularly useful for the Hubbard model. In the Hubbard model [31], the transport limit and the high frequency limit are on opposite sides of a crucial energy scale U . More explicitly, a large $\omega \gg U$ is implicit in this limit and therefore deals with weakly renormalized particles. We expect it to differ from the transport limit $\omega \rightarrow 0$ significantly in qualitative terms, such as the signs of carriers and the Hall number.

It is worthwhile recording a dispersion relation for the Hall constant at this point. Since $R_H(\omega)$ is analytic in the upper half of the complex ω plane, and has a finite limit at infinite ω , we may write

$$R_H(\omega) = R_H^* - \int_{-\infty}^{\infty} \frac{dv}{\pi} \frac{\Im m R_H(v)}{\omega - v + i0^+}, \quad (10)$$

therefore in the dc limit we get

$$\Re e R_H(0) = R_H^* + \frac{2}{\pi} \int_0^{\infty} \frac{\Im m R_H(v)}{v} dv. \quad (11)$$

This equation quantifies the difference between the experimentally measured dc-Hall coefficient and the theoretically more accessible infinite frequency limit. The second term is an independently measurable object, and initial measurements of this are now available in [32]. It would be very useful to make a systematic study of this promising dispersion relation, both theoretically and experimentally. For the case of the square lattice systems, the theoretical estimates of the difference are indicated in figure 1 for a couple of densities. We plan to return to this rich topic in future studies.

As an illustration of the above formalism, we note that a recent work on the triangular lattice system Na_xCoO_2 provides a good example. Theoretically, the ‘exotic’ prediction, namely, that the Hall constant grows linearly with temperature T on a triangular lattice, was first recognized in 1993 [25]. This behaviour arises for $T \geq T_{\text{Fermi}}$. On the other hand, for low temperatures, it is expected to be less sensitive to T , as in a Fermi liquid. This prediction arises in a simple way from equation (7) treated within the high temperature expansion [25, 30]. The numerator is dominated by the shortest closed loops of electron hopping that encircle a flux, and these are, of course, triangles for the triangular lattice. This leads at

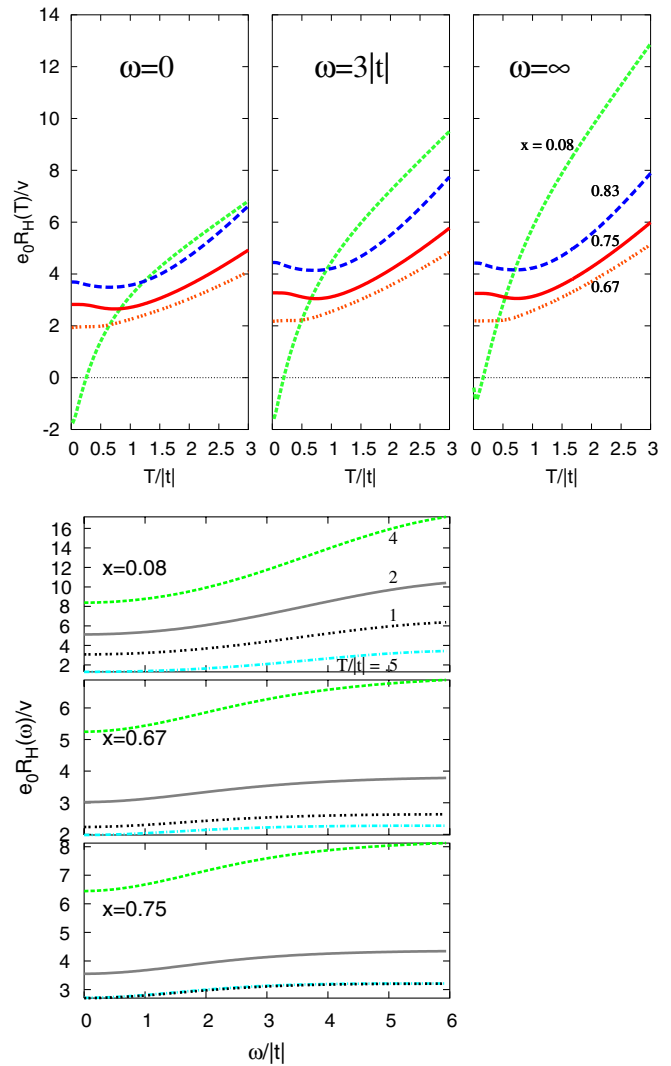


Figure 1. Frequency dependence of the Hall coefficient on the triangular lattice from computation on small clusters of the t – J model [29, 35] for electron doping x . The values of doping x are indicated in the figures. In the upper figure, the linear T dependence is striking in all cases. The bottom figure displays the frequency dependence for various values of x and T . It is seen from these curves that frequency dependence is modest except for the case of very low doping. Reprinted with permission from [35]b. Copyright 2006 by the American Physical Society.

high T (or small inverse temperature β) to the numerator $\propto \beta$ whereas the denominator is always $\propto \beta^2$ and hence a T linear Hall constant with a well-defined coefficient

$$R_H^* = -\frac{v}{4|q_e|} \frac{k_B T}{t} \frac{1 + \delta}{\delta(1 - \delta)} + c_1 + \frac{c_2}{T} + \dots \quad (12)$$

This result (with suitable constants c_1, c_2) [30] is for the experimentally relevant case of electron filling so that $\delta = (N/N_s) - 1$ and has a suitable counterpart for the case of hole filling. It is remarkable in two distinct ways. Firstly, it shows that the sign of the Hall constant is not universal, as one might naively expect from the Sommerfeld Drude theory formula $R_H = 1/nq_e c$. Rather it depends upon the *sign of the hopping* as well. This aspect was recognized in the important work of Holstein [33], within the context of hopping conduction in

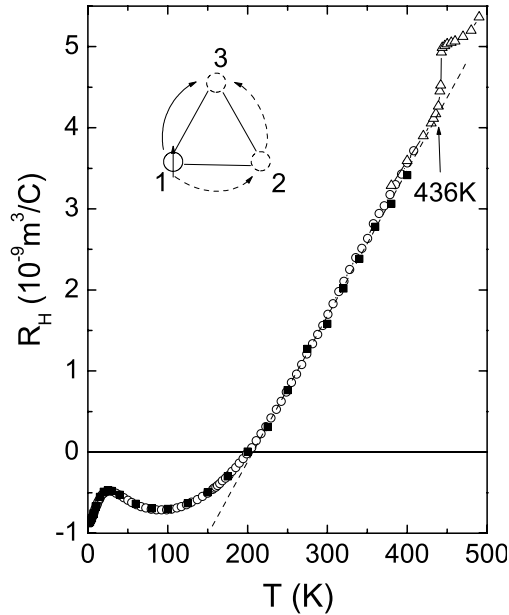


Figure 2. Experimental temperature dependence [34] of the Hall coefficient of sodium cobaltate $\text{Na}_{0.68}\text{CoO}_2$ over a broad range of temperatures. The sample is in the so-called Curie–Weiss metallic phase. The inset stresses the crucial role of the triangular closed loops in giving rise to the surprising behaviour.

doped semiconductors. The other remarkable feature is that the Hall resistivity increases linearly with T , a result first found in [25, 30]⁴. The final answer is therefore highly non-universal and depends upon material parameters such as the magnitude and sign of the hopping and also the nature of the doping (holes versus electron). We reiterate that this asymptotic behaviour is obtained provided $k_B T \geq |t|$ and as such is experimentally observable only for narrow band systems. In general, from equation (7) one expects a T independent Hall constant for T sufficiently below a (usually large) characteristic Fermi temperature, as in most metallic systems.

Interestingly enough, the case of Na_xCoO_2 with $x \sim 0.68$, i.e. the so-called Curie–Weiss metallic phase, seems to fulfill these conditions of narrow bandwidth. As figure 2 shows, the experiments show a large and clear-cut region of linear T dependence [34], thereby fulfilling the basic theoretical prediction of equation (12). Recent work [35] attempts to reconcile many experimental results in this phase, including the Hall constant coefficient of T , with the theoretical predictions. Many experiments such as the photoemission quasiparticle velocities, the magnetic susceptibility and specific heat are understandable with $|t|/k_B \sim 100$ K (i.e. a bare band width $9|t| \sim 10^{-2}$ eV). At $x = 0.68$, the Hall slope requires a smaller value $|t|/k_B \sim 25$ K, but nearby compositions seem to have a smaller slope translating to a larger value of $|t|/k_B$ that is more in line with the other data. All these numbers are, in turn, much smaller than LDA estimates of the bandwidth of 0.2 eV [36] by an order of magnitude and pose an interesting

⁴ Using a semiclassical theory of transport, Holstein estimated the Hall conductivity and Hall angle σ_{xy}/σ_{xx} , rather than the Hall resistivity as in equation (12). The neat prediction [25, 30] of a T linear behaviour (equation (12)) emerges only for the Hall resistivity, where many factors cancel out.

problem to the community. In this review, our interest in the Hall constant of the cobaltates is mostly motivational and hence tangential; we will leave this topic for further work. In the case of the cuprates, the work in [25, 29] shows that R_H^* provides a useful first principles estimate for the physical (dc) transport Hall constant $R_H(0)$ for correlated systems. Our task in these notes is to carry this message to the computation of the thermal response functions, and so we terminate our discussion of the interesting problem of the Hall constant.

3. Thermoelectric response

We next address the main topic of this paper, namely, the thermal response functions. In light of the previous discussion of the Hall constant, we searched for the analogue of R_H^* . Therefore, we needed the finite (high) frequency limits of thermal response functions. To the author's surprise, these limiting functions were unavailable in the literature, therefore leading to the basic calculation in [37]. We begin with a quick review of the standard transport theory given in many texts [9, 10, 26, 38, 39]. We write down the set of linear response equations following Onsager [38]:

$$\frac{1}{\Omega} \langle \hat{J}_x \rangle = L_{11} E_x + L_{12} (-\nabla_x T/T), \quad (13)$$

$$\frac{1}{\Omega} \langle \hat{J}_x^Q \rangle = L_{21} E_x + L_{22} (-\nabla_x T/T), \quad (14)$$

where $(-\nabla_x T/T)$ is regarded as the *external driving thermal force* [9, 38, 40]. The operator \hat{J}_x is the total charge current operator and has been defined earlier in equation (4). Further \hat{J}_x^Q is the heat current operator defined as $\hat{J}_x^Q = \lim_{q_x \rightarrow 0} (1/q_x) [K, K(q_x)]$, where $K(q_x)$ is the Fourier component of the grand canonical Hamiltonian density (equation (18)) and $\lim_{q_x \rightarrow 0} K(q_x) = K$. These variables are elaborated upon below in equations (34) and (35) and $\Omega = \nu N_s$ is the total volume of the system. The parameter L_{11} is related to the dc conductivity $\sigma(0) = L_{11}^5$, the parameter L_{12} is related⁶ to the Seebeck coefficient

$$S = \frac{L_{12}}{T L_{11}}, \quad (15)$$

also L_{21} is related to the Peltier coefficient

$$\Pi = L_{21}/L_{11} = T S, \quad (16)$$

the final equality in equation (16) relating the Peltier and Thomson effects is the celebrated reciprocity due to Thomson (Kelvin) [40] and Onsager [38]. It is most compactly written as $L_{12} = L_{21}$. The Onsager constant L_{22} is related to the (nominal) thermal conductivity $\kappa = (1/T)L_{22}$ for problems with immobile degrees of freedom (spins, ions, etc). For metallic systems, however, the observed thermal conductivity κ_{zc} requires a small correction (see equation (17)). The usually observed thermal conductivity [10, 26, 28] uses

⁵ Our definition includes the volume factor and this makes L_{11} identical to the (intensive) conductivity.

⁶ Sometimes in the literature [9, 10, 26], S is denoted by Q .

the zero electrical current condition $\langle \hat{J}_x \rangle = 0$, thereby inducing an electric field. The generated electric field is related by equation (13) to the applied thermal force, and using it in equation (14) we find the zero current thermal conductivity [10, 26]

$$\kappa_{zc} = \frac{1}{TL_{11}}(L_{22}L_{11} - L_{12}L_{21}). \quad (17)$$

These are equations in the static limit and correspond to the most simple non-equilibrium states with a steady current flow.

3.1. Luttinger's gravitational field analogy

In order to generalize the above transport theory to finite frequencies, we need to borrow a beautiful idea from Luttinger [39]. In order to derive the Kubo formulae [41], he introduces the mechanical equivalent of the thermal gradient, and we shall use it extensively. The fictitious mechanical field $\psi(\vec{x}, t)$ is similar to a gravitational field, coupling to the effective 'mass density' $m_{\text{eff}}(\vec{x}) = (1/c^2)K(\vec{x})$ via

$$K_{\text{tot}} = K + \sum_x K(\vec{x})\psi(\vec{x}, t). \quad (18)$$

Here $K = \sum_x K(\vec{x})$ and $K(\vec{x}) = H(\vec{x}) - \mu n(\vec{x})$ is the Grand canonical Hamiltonian⁷, $H(\vec{x})$, $n(\vec{x})$, μ are the local canonical ensemble Hamiltonian, number density and chemical potential. Below, we will expand $K(\vec{x}) = \frac{1}{\Omega} \sum \exp -i\vec{q} \cdot \vec{x} K(\vec{q})$, with a similar expansion for the charge and other densities and currents. We can compute the standard linear response to a space-time dependent $\psi(\vec{x}, t)$, and with the help of the ideas initiated by Luttinger deduce the dynamical thermal response functions required in equation (37).

Firstly, let us note that the local temperature $\delta T(\vec{x}, t)$ can be defined in the long wavelength almost static limit through small departures from equilibrium. The local energy fluctuation can be written as $\langle K(\vec{x}, t) \rangle = \langle K \rangle_0 + C(T) \delta T(\vec{x}, t)$, with $C(T)$ as the specific heat at the equilibrium temperature T (at constant volume and μ), provided $\delta T(\vec{x}, t) \ll T$. Hence we can invert to define the local temperature through

$$\delta T(\vec{x}, t) = \frac{\delta \langle K(\vec{x}, t) \rangle}{C(T)}. \quad (19)$$

The connection of $\psi(\vec{x}, t)$ with local temperature $\delta T(\vec{x}, t)$ emerges from a study of the generalized phenomenological equations proposed by Luttinger [39]. He focuses on long wavelength $\vec{q} \rightarrow 0$ and static $\omega \rightarrow 0$ limits where equilibrium is rigorously definable; we will extend this notion to arbitrary variations. The phenomenological relations are generalizations of the Onsager formulation [38] as in equations (13) and (14) and correspond to adding terms

⁷ The need for introducing the Grand canonical Hamiltonian K lies in the construction of the heat current operator \hat{J}_x^Q , where the particle current must be subtracted from the energy current (equation (34)).

proportional to the gradient of the mechanical term $\propto \psi$ in equation (18). Luttinger writes

$$\frac{1}{\Omega} \langle \hat{J}_x \rangle = L_{11} E_x + L_{12} (-\nabla_x T/T) + \hat{L}_{12} (-\nabla_x \psi(\vec{x}, t)), \quad (20)$$

$$\frac{1}{\Omega} \langle \hat{J}_x^Q \rangle = L_{21} E_x + L_{22} (-\nabla_x T/T) + \hat{L}_{22} (-\nabla_x \psi(\vec{x}, t)), \quad (21)$$

where the two new response functions \hat{L}_{12} , \hat{L}_{22} are functions of space and time which can be readily computed from a linear response theory treatment of the mechanical perturbation in equation (18). We will treat ψ as a small perturbation and work to linear order here. Addition of the ψ term in these equations allows us to take a different perspective⁸. In equations (20) and (21) we can view the driving term as ψ , with the temperature fluctuation arising as a consequence of this driving, at least for long wavelengths and slow variations⁹.

In these equations (20) and (21), the idea is to determine the difficult unknowns L_{12} , L_{22} in terms of the easier objects \hat{L}_{12} , \hat{L}_{22} . Let us consider one particular example for simplicity, the others follow similarly. Since the theory is linear in the external perturbation, it suffices to consider a single frequency and wave vector mode. Therefore, let us focus on equation (20), and introduce a single Fourier component $\psi(\vec{x}, t) = \psi_q \exp\{-i(q_x x + \omega t + i0^+ t)\}$, (adiabatic switching implied) and the electric potential $\phi(\vec{x}, t) = \phi_q \exp\{-i(q_x x + \omega t + i0^+ t)\}$. We thus write

$$\frac{1}{\Omega} \delta \hat{J}_x = L_{11}(q_x, \omega)(iq_x)\phi_q + (iq_x) \left[L_{12}(q_x, \omega) \frac{\delta T_q}{T} + \hat{L}_{12}(q_x, \omega)\psi_q \right], \quad (22)$$

where $\langle \hat{J}_x(\vec{x}) \rangle = (1/\Omega)\delta J_x \exp -i(q_x x + \omega t)$, so that δJ_x is the amplitude of the response, and we have written the arguments of the Onsager-Luttinger functions L_{ij} , \hat{L}_{ij} explicitly.

To be explicit, we define two extreme limits of \vec{q} and ω that arise here [39], one is the so-called rapid or transport limit,

⁸ Note that experiments usually employ *open boundary conditions*, and the temperature gradient is externally applied. The usual argument made is that the periodic boundary case and the open boundary case are equivalent, provided we take the wave vector $\vec{q} \rightarrow 0$ or the thermodynamic volume $\Omega \rightarrow \infty$ limits, respectively, while keeping the frequency ω finite and small. This gives a prescription for the dc limit in both cases, namely, to take the dc limit at the end of the volume (or wave vector) limits (equations (13) and (14)).

⁹ This is where Luttinger uses the tactical analogy with the Einstein relation for the relationship between self-diffusion and conductivity. In the phenomenological equation $\langle \hat{J}_x \rangle = \sigma E_x + D(-\nabla_x)\langle \rho \rangle$, the driving term is E_x . In equation (20) (neglecting the L_{11} term for a moment), the ψ term is analogous to the E_x in the diffusion problem, and the induced temperature variation is similar to the induced charge fluctuation. For completeness, we summarize Luttinger's argument for this case. For small wave vectors and slow variation of the electric field $E_x = -\nabla\phi(x) = E_0 \exp -i(q_x x + \omega t)$. Upon using the continuity equation $\langle \rho_q \rangle = -(q_x/\omega)\langle \hat{J}_x \rangle$ we see that $\langle \hat{J}_x \rangle = \sigma E_0(\omega/(\omega + iDq_x^2))$. Similarly the charge fluctuation $\langle \rho_q \rangle = \sigma\phi_q(-iq_x^2/(\omega + iDq_x^2))$, where $\phi_q = -iE_0/q_x$. Luttinger's argument is that in the fast or transport limit $\omega \rightarrow 0$, $q_x \rightarrow 0$ so that the diffusion term can be dropped. However, in the slow limit, the relations derived above show that $(\sigma/D) = -\langle \rho_q \rangle / \langle \phi_q \rangle$. The right-hand side of this is easily computed from *thermodynamics*, whereby the Einstein relation $\sigma/D = e^2/(\partial\mu/\partial n)_T$ follows.

and the other is the slow or the thermodynamic limit. In the rapid or transport limit, we first let $q_x \rightarrow 0$ and then let ω vanish. In the slow limit, we set $\omega \rightarrow 0$ first and then take the limit $q_x \rightarrow 0$.

In the transport limit, we have a spatially uniform field, and hence we can show that $\delta T_q \rightarrow 0$. This is most easily seen by inspecting the continuity equation for heat density and current in the absence of an external heating source: $\omega \langle K_q \rangle + q_x \langle \hat{J}_x^Q \rangle = 0$. This can be written using equation (19) as $\delta T_q = (-q_x/C(T) \omega) \langle \hat{J}_x^Q \rangle$. Thus dropping the δT_q term, we find

$$\frac{1}{\Omega} \delta \hat{J}_x = L_{11}(0, \omega) \lim_{q_x \rightarrow 0} (iq_x) \phi_q + \hat{L}_{12}(0, \omega) \lim_{q_x \rightarrow 0} (iq_x) \psi_q. \quad (23)$$

The object $\lim_{q_x \rightarrow 0} (iq_x) \phi_q \rightarrow E_x$ and likewise for the gravitational term, and hence this equation is essentially the same as equation (20).

On the other hand, in taking the slow limit, with $\omega \rightarrow 0$, the system is subject to a time independent but a spatially varying gravitational potential as well as a temperature gradient; this is now an equilibrium problem without a net current. Thus $\langle \hat{J}_x(q_x) \rangle = 0$, leading to

$$0 = L_{12}(q, 0) \frac{\delta T_q}{T} + \hat{L}_{12}(q, 0) \psi_q. \quad (24)$$

In this equilibrium situation, we can compute the connection between $\delta T_q/T$ and ψ_q readily. Using lowest order thermodynamic perturbation theory [10, 42] we compute the change in energy induced by a small perturbation ψ_q

$$\frac{\delta \langle K(\vec{q}) \rangle}{\psi_q} = - \sum \frac{p_n - p_m}{\epsilon_m - \epsilon_n} | \langle n | K(\vec{q}) | m \rangle |^2 + O(\psi), \quad (25)$$

with $p_n = (1/Z) \exp(-\beta \epsilon_n)$ the probability of the state n . In the limit $\vec{q} \rightarrow 0$, $K(\vec{q})$ tends to the Hamiltonian, and hence cannot mix states of different energy; hence we write $\lim_{\epsilon_m \rightarrow \epsilon_n} (p_n - p_m)/(\epsilon_m - \epsilon_n) \rightarrow \beta p_n$, whereby

$$\lim_{\vec{q} \rightarrow 0} \frac{\delta \langle K(\vec{q}) \rangle}{\psi_q} \rightarrow -\beta [\langle K^2 \rangle - \langle K \rangle^2] \quad (26)$$

$$= -TC(T). \quad (27)$$

This calculation is parallel to that in the literature [43] for the electron liquid, where the dielectric function is related to the compressibility in the limit of $\vec{q} \rightarrow 0, \omega \rightarrow 0$. Comparing the final equation (27) with the standard thermodynamic definition of $C(T)$, we see that

$$\lim_{q \rightarrow 0} \frac{\delta \langle K(\vec{q}) \rangle}{\psi_q} = -T \frac{d}{dT} \langle K \rangle, \quad (28)$$

whereby

$$\lim_{\vec{q} \rightarrow 0} \psi_q = - \lim_{\vec{q} \rightarrow 0} \frac{\delta T_q}{T}. \quad (29)$$

Comparing equations (29) and (24), we see that

$$\lim_{q \rightarrow 0} [L_{12}(q, 0) - \hat{L}_{12}(q, 0)] = 0. \quad (30)$$

From this relation, Luttinger concludes that L_{12} in the dc limit can be computed from \hat{L}_{12} . Thus the problem of computing

thermal response is reduced to computing the mechanical response to the field $\psi(\vec{x}, t)$ and essentially treating¹⁰ the $\lim_{\vec{q} \rightarrow 0} \psi_q = \lim_{\vec{q} \rightarrow 0} (\delta T_q/T)$.

This is undoubtedly huge progress. However, as far as I can make out, this fine proof of Luttinger makes another implicit assumption, namely, that

$$\lim_{\omega \rightarrow 0} [L_{12}(0, \omega) - \hat{L}_{12}(0, \omega)] = 0 \quad (31)$$

somehow follows from equation (30). This is assumed so despite the fundamental difference in the two limits, namely, the slow (thermodynamic) and fast (transport) limits. The belief thus seems to be that the two functions L_{ij} and \hat{L}_{ij} must be identical in the fast limit, if they are so in the slow limit.

In this work we need to define finite q, ω thermal response functions. Towards this end, we will in fact *extend the above to all q, ω* , and simply assume that

$$L_{ij}(q, \omega) = \hat{L}_{ij}(q, \omega). \quad (32)$$

The RHS is computable within perturbation theory, and the LHS, although defined rigorously only in the regime of small q, ω by hydrodynamic type reasoning, is extended to all q, ω by this relation. This idea of extending the thermal functions seems reasonable, since the resulting functions agree with hydro-thermodynamics for small q, ω and are guaranteed to satisfy general properties such as causality and Onsager reciprocity. With this, we can define all thermal response functions at all q, ω , and in the following we will work within this generalized Luttinger viewpoint.

3.2. Finite ω thermal response functions

With this preparation, we return to exploring the thermal response (equation (37)) at finite frequencies. The timing of our quest seems fortuitous, since there is growing experimental interest in the transport of energy and heat pulses, requiring knowledge of these variables and of the approach to equilibrium.

We first need to define the heat current \hat{J}_x^Q . Towards this end, we take the time derivative of the first law of thermodynamics for fixed volume $T(dQ/dt) = (dE/dt) - \mu(dn/dt)$. Imagining a small volume with the flow of energy and heat as well as density, and applying this law locally, it is reasonable to identify the heat current as the energy current minus the particle current (times μ). Thus the heat current can be decomposed as the difference in two terms:

$$\hat{J}_x^Q = \hat{J}_x^E - \frac{\mu}{q_e} \hat{J}_x, \quad (33)$$

where \hat{J}_x^E is the *energy current* and \hat{J}_x the *charge current*. In a quantum mechanical system, the heat current operator is most

¹⁰ The alert reader would have noted that this assignment has an opposite sign to equation (29). The explanation for this slight 'booby trap' is that in equation (29), the gravitational field and the thermal gradient are simultaneously present in order to cancel the current. Their relative sign is therefore negative. In making the suggested replacement, the gravitational field is used *as a proxy* for the temperature gradient, and hence the relative sign is reversed from the earlier context.

easily computed from the commutator of the energy density operator with total energy as follows (setting $\hbar = 1$):

$$\hat{J}_x^Q = \lim_{q_x \rightarrow 0} \frac{1}{q_x} [K, K(q_x)]. \quad (34)$$

This construction is similar to the more familiar one for the charge current $\hat{J}_x = \lim_{q_x \rightarrow 0} (1/q_x) [K, \rho(q_x)]$. By inspection, a local heat current operator can also be written down provided the interactions are local, so that we can take Fourier components in a periodic box¹¹ and write

$$\hat{J}_x^Q(\vec{q}) = v \sum_x \hat{J}_x^Q(\vec{x}) \exp(i\vec{q} \cdot \vec{x}) \quad \text{and}$$

$$\hat{J}_x(\vec{q}) = v \sum_x \hat{J}_x(\vec{x}) \exp(i\vec{q} \cdot \vec{x}). \quad (35)$$

Therefore, $\hat{J}_x^Q = \hat{J}_x^Q(\vec{0})$ and $\hat{J}_x = \hat{J}_x(\vec{0})$. For different models, the heat current is easy to compute using the above prescription, and many standard models are treated in [37].

Let us impose fields that vary as $\psi(\vec{x}, t) = \psi_q \exp[-i(q_x x + \omega t + i0^+ t)]$, and similarly for the electric field with the electric potential $\phi(\vec{x}, t) = \phi_q \exp[-i(q_x x + \omega t + i0^+ t)]$. Using the notation $\langle \hat{J}_x(q_x) \rangle = \delta J_x$ and $\langle \hat{J}_x^Q(q_x) \rangle = \delta J_x^Q$, we find from equations (20), (21) that

$$\frac{1}{\Omega} \delta J_x = L_{11}(q_x, \omega)(iq_x \phi_q) + L_{12}(q_x, \omega)(iq_x \psi_q), \quad (36)$$

$$\frac{1}{\Omega} \delta J_x^Q = L_{21}(q_x, \omega)(iq_x \phi_q) + L_{22}(q_x, \omega)(iq_x \psi_q). \quad (37)$$

These responses are to be computed for a Hamiltonian perturbed by a single Fourier component as

$$K_{\text{tot}} = K + [\rho(-q_x) \phi_q + K(-q_x) \psi_q] \exp(-i\omega t + 0^+ t), \quad (38)$$

where $\rho(\vec{q})$ is the charge density fluctuation operator at wave vector \vec{q} .

We can reduce the calculations of all L_{ij} to essentially a single one, with the help of some notation. Keeping q_x small but non-zero, we define currents, densities and forces in a matrix notation as follows:

$i = 1$	$i = 2$	
Charge	Energy	
\mathcal{I}_i	$\hat{J}_x(q_x)$	$\hat{J}_x^Q(q_x)$
\mathcal{U}_i	$\rho(-q_x)$	$K(-q_x)$
\mathcal{Y}_i	$E_q^x = iq_x \phi_q$	$iq_x \psi_q$

$$(39)$$

The perturbed Hamiltonian equation (38) can then be written as

$$K_{\text{tot}} = K + \sum_j Q_j e^{-i\omega_c t}, \quad \text{where } Q_j = \frac{1}{iq_x} \mathcal{U}_j \mathcal{Y}_j. \quad (40)$$

¹¹ We imagine doing this calculation on a lattice; therefore the Fourier transforms are written as sums over sites, with a factor of the atomic volume v inserted for keeping track of dimensions.

We denote $\omega_c = \omega + i0^+$ above and elsewhere. From standard linear response theory [39] applied to equation (40), we readily extract the induced current response

$$\langle \mathcal{I}_i \rangle = - \sum_j \chi_{\mathcal{I}_i, Q_j}(\omega_c), \quad (41)$$

where the susceptibility for any two operators $\chi_{A,B}(\omega_c)$ can be expressed as (with $A_{nm} \equiv \langle n|A|m \rangle$)

$$\begin{aligned} \chi_{A,B}(\omega_c) &= i \int_0^\infty dt e^{i\omega t - 0^+ t} \langle [A(t), B(0)] \rangle \\ &= \sum_{n,m} \frac{p_m - p_n}{\varepsilon_n - \varepsilon_m + \omega_c} A_{nm} B_{mn} \\ &= -\frac{1}{\omega_c} \left[\langle [A, B] \rangle + \sum_{n,m} \frac{p_m - p_n}{\varepsilon_n - \varepsilon_m + \omega_c} \right. \\ &\quad \left. \times A_{nm} ([B, K])_{mn} \right]. \end{aligned} \quad (42)$$

The last line of equation (42) follows from integration by parts of the first line, and the average $\langle \rangle$ is carried out over the ensemble where the external fields are dropped.

From equation (41), using the notation in equations (39) and (42), the generalized Onsager coefficients

$$L_{ij}(q_x, \omega) = \frac{1}{\Omega} \lim_{\mathcal{Y}_j \rightarrow 0} \langle \mathcal{I}_i \rangle / \mathcal{Y}_j. \quad (43)$$

are written down immediately:

$$\begin{aligned} L_{ij}(q_x, \omega) &= \frac{1}{i\Omega\omega_c} \left[\langle [\mathcal{I}_i, \mathcal{U}_j] \rangle \frac{1}{q_x} \right. \\ &\quad \left. + \frac{1}{q_x} \sum_{n,m} \frac{p_m - p_n}{\varepsilon_n - \varepsilon_m + \omega_c} (\mathcal{I}_i)_{nm} ([\mathcal{U}_j, K])_{mn} \right]. \end{aligned} \quad (44)$$

We now record the continuity equation for energy and charge. These can be compactly written in Fourier space, for small q and in the absence of external energy sources. Using the definitions in equation (39), we find $[\mathcal{U}_j, K] = q_x \mathcal{I}_j^\dagger$. Therefore

$$\begin{aligned} L_{ij}(q_x, \omega) &= \frac{i}{\Omega\omega_c} \left[-\langle [\mathcal{I}_i, \mathcal{U}_j] \rangle \frac{1}{q_x} \right. \\ &\quad \left. - \sum_{n,m} \frac{p_m - p_n}{\varepsilon_n - \varepsilon_m + \omega_c} (\mathcal{I}_i)_{nm} (\mathcal{I}_j^\dagger)_{mn} \right]. \end{aligned} \quad (45)$$

We next proceed to take the limit of small q_x . Here the inconvenient-looking first term in equation (45) tends to a finite limit in *all cases*, owing to a simple but important point. We first note that for a large system, $K(-q_x)$ tends continuously to the Hamiltonian K in the limit $q_x \rightarrow 0$. We further note that for a generic operator P , the cyclicity of trace yields

$$\langle [P, K] \rangle = \frac{1}{\mathcal{Z}} \text{Trace}[e^{-\beta K} (PK - KP)] \equiv 0. \quad (46)$$

This relation is noted as Identity-I in [37]. It follows that $\langle [P, K(-q_x)] \rangle \propto q_x$ with a well-defined coefficient [37]. Consulting the list of variables in equation (39), we conclude that $\lim_{q_x \rightarrow 0} \langle [\mathcal{I}_i, \mathcal{U}_j] \rangle = 0$ in all cases of interest. Observe that

this result *does not require the vanishing of the commutator* $[P, K]$. In the case of thermal transport L_{22} , this point is important since the heat current does not commute with the Hamiltonian. In contrast, for L_{11} , i.e. electrical transport, the charge current commutes with the total number operator and hence the limit of the ratio is well defined more trivially, leading to the familiar f-sum rule as shown below.

In the uniform limit $q_x \rightarrow 0$, and hence from equation (39) we can set $\mathcal{I}_j^\dagger = \mathcal{I}_j$. Therefore for arbitrary frequencies, the Onsager functions read as

$$L_{ij}(\omega) = \frac{i}{\Omega\omega_c} \left[\langle \mathcal{T}_{ij} \rangle - \sum_{n,m} \frac{p_m - p_n}{\varepsilon_n - \varepsilon_m + \omega_c} (\mathcal{I}_i)_{nm} (\mathcal{I}_j)_{mn} \right], \quad (47)$$

$$\langle \mathcal{T}_{ij} \rangle = - \lim_{q_x \rightarrow 0} \langle [\mathcal{I}_i, \mathcal{U}_j] \rangle \frac{1}{q_x} = - \lim_{q_x \rightarrow 0} \frac{d}{dq_x} \langle [\mathcal{I}_i, \mathcal{U}_j] \rangle. \quad (48)$$

The operators \mathcal{T}_{ij} are not unique, since one can add to them a ‘gauge operator’ $\mathcal{T}_{ij}^{\text{gauge}} = [P, K]$ with arbitrary P , without affecting the thermal average, due to Identity-I (equation (46)) discussed above. These fundamental operators play a crucial role in the subsequent analysis, since they determine the high frequency behaviour of the response functions. These important operators are written in a more familiar representation [37] as follows.

Stress tensor	Thermal operator	Thermoelectric operator
\mathcal{T}_{11}	\mathcal{T}_{22}	$\mathcal{T}_{12} = \mathcal{T}_{21}$
τ^{xx}	Θ^{xx}	Φ^{xx}
$-\frac{d}{dq_x} [\hat{J}_x(q_x), \rho(-q_x)]_{q_x \rightarrow 0}$	$-\frac{d}{dq_x} [\hat{J}_x^Q(q_x), K(-q_x)]_{q_x \rightarrow 0}$	$-\frac{d}{dq_x} [\hat{J}_x(q_x), K(-q_x)]_{q_x \rightarrow 0}$

The thermoelectric operator can also be written as

$$\Phi^{xx} = \mathcal{T}_{21} = - \frac{d}{dq_x} [\hat{J}_x^Q(q_x), \rho(-q_x)]_{q_x \rightarrow 0}, \quad (50)$$

and its equivalence to the form given in equation (49) amounts to showing $\mathcal{T}_{12} = \mathcal{T}_{21}$, modulo the addition of a ‘gauge operator’ discussed above. This task is more non-trivial than one might naively anticipate and requires the use of Jacobi’s identity as discussed later.

Several aspects of equations (47) and (49) are worth mentioning at this point.

3.3. Onsager reciprocity at finite frequencies

We first note that the celebrated reciprocity relations of Onsager are extended to finite ω here. These require in the present case (with no magnetic fields)

$$L_{ij}(\omega) = L_{ji}(\omega). \quad (51)$$

One part of the above dealing with the second term of equation (47) goes back to Onsager’s famous argument: in the absence of a magnetic field we can choose a real phase

convention for the quantum wave functions such that the product $(\mathcal{I}_i)_{nm} (\mathcal{I}_j)_{mn}$ is real. Invariance under complex conjugation then implies invariance under the exchange $i \leftrightarrow j$.

The full (frequency dependent) function shows reciprocity only if we can show that $\mathcal{T}_{ij} = \mathcal{T}_{ji}$, since this is the first part of equation (47). This identity requires the use of the Jacobi identity $0 = [[a, b], c] + [[c, a], b] + [[b, c], a]$ for any three operators a, b, c and can be proved as follows. Consider \mathcal{T}_{12} which requires the first order term in q of the expectation of $[\hat{J}_x(q), K(-q)]$. Now we use $\hat{J}_x(q) = 1/q[K, \rho(q)]$ to lowest order in q , so that

$$\langle \mathcal{T}_{12} \rangle = - \left(\frac{d}{dq} \frac{1}{q} \langle [[K, \rho(q)], K(-q)] \rangle \right)_{q \rightarrow 0} \quad (52)$$

$$= \left(\frac{d}{dq} \frac{1}{q} \langle [[\rho(q), K(-q)], K] + [K(-q), K], \rho(q)] \rangle \right)_{q \rightarrow 0} \quad (53)$$

$$= \left(\frac{d}{dq} \langle [[\hat{J}_x^Q(-q), \rho(q)]] \rangle \right)_{q \rightarrow 0} \quad (54)$$

$$= \langle \mathcal{T}_{21} \rangle. \quad (55)$$

We used Jacobi’s identity to go to equation (53) from equation (52) and dropped the first term in equation (53) using Identity-I 46. Equation (54) follows on using the definition of the heat current (equation (34)). Thus we have *reciprocity for all ω* . A generalization to include magnetic fields can be readily made, but we skip it here.

3.4. General formulae for $L_{ij}(\omega)$

We start with equation (47). By using a simple algebraic identity with partial fractions for arbitrary Δ [37], we write

$$\frac{1}{\hbar\omega_c(\hbar\omega_c + \Delta)} = \frac{1}{\Delta} \left(\frac{1}{\hbar\omega_c} - \frac{1}{\hbar\omega_c + \Delta} \right);$$

we obtain

$$L_{ij}(\omega_c) = \frac{i}{\omega_c} \mathcal{D}_{ij} + \frac{i}{\Omega} \sum_{n,m} \frac{p_n - p_m}{\varepsilon_m - \varepsilon_n} \frac{(\mathcal{I}_i)_{nm} (\mathcal{I}_j)_{mn}}{\varepsilon_n - \varepsilon_m + \hbar\omega_c}. \quad (56)$$

where

$$\mathcal{D}_{ij} = \frac{1}{\Omega} \left[\langle \mathcal{T}_{ij} \rangle - \sum_{nm} \frac{p_n - p_m}{\varepsilon_m - \varepsilon_n} (\mathcal{I}_i)_{nm} (\mathcal{I}_j)_{mn} \right]. \quad (57)$$

At this point it is useful to follow Kubo [41] and introduce imaginary time operators $Q(\tau) \equiv e^{\tau K} Q e^{-\tau K}$, where $0 \leq \tau \leq \beta$. A simple exercise in inverse Lehmann representation¹² of the above equations (56) and (57) gives us the following compact Kubo type expressions [37, 41] for the generalized conductivities:

$$L_{ij}(\omega) = \frac{i}{\omega_c} \mathcal{D}_{ij} + \frac{1}{\Omega} \int_0^\infty dt e^{i\omega_c t} \int_0^\beta d\tau \langle \mathcal{I}_i(t - i\tau) \mathcal{I}_j(0) \rangle, \quad (58)$$

$$\mathcal{D}_{ij} = \frac{1}{\Omega} \left[\langle \mathcal{T}_{ij} \rangle - \int_0^\beta d\tau \langle \mathcal{I}_i(-i\tau) \mathcal{I}_j(0) \rangle \right]. \quad (59)$$

¹² Pedagogically it might be easier to go in the opposite direction and to insert a complete set of eigenfunctions of K in equations (58) and (59), followed by a simple integration over the imaginary time.

The stiffnesses D_{ij} are discussed in detail in [37] and are in general non-zero for all non-dissipative systems such as superfluids and superconductors. For a superconductor D_{11} is the Meissner stiffness, so that the superfluid density can be defined in terms of it [37]. In a superfluid or a highly pure crystal supporting second sound, the stiffness D_{22} is non-zero and related to the second sound phenomenon. For dissipative systems, these stiffnesses vanish, and on dropping them from equation (58) we get back the familiar Kubo type formulae [39, 41].

3.5. High frequency behaviour

The high frequency behaviour of these functions is easily found from equation (47) as

$$\lim_{\omega \gg 0} L_{ij}(\omega) = \frac{i}{\omega\Omega} \langle \mathcal{T}_{ij} \rangle + O(1/\omega^2). \quad (60)$$

Thus these fundamental operators determine the high frequency response, and we will pursue the consequences later.

3.6. Sum rules for electrical and thermal conductivity

It is worth noting that these relations imply sum rules as well, for the thermal response functions. To see this, note that the causal nature of the Onsager coefficients and an asymptotic fall-off as inverse frequency provides a dispersion relation, i.e. a Kramers–Kronig relation, where \mathcal{P} represents the principal value of the integral,

$$\Re L_{ij}(\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{d\nu}{\nu - \omega} \Im L_{ij}(\nu), \quad (61)$$

$$\Im L_{ij}(\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{d\nu}{\omega - \nu} \Re L_{ij}(\nu). \quad (62)$$

We see at high frequencies from equations (60) and (62) and assuming the reality of the averages $\langle \mathcal{T}_{ij} \rangle$:

$$\lim_{\omega \gg 0} \omega \Im L_{ij}(\omega) = \frac{\langle \mathcal{T}_{ij} \rangle}{\Omega} = \int_{-\infty}^{\infty} \frac{d\nu}{\pi} \Re L_{ij}(\nu). \quad (63)$$

This relation gives all the interesting sum rules in this problem. More explicitly we find

$$\int_{-\infty}^{\infty} \frac{d\nu}{2} \Re \sigma(\nu) = \frac{\pi \langle \tau^{xx} \rangle}{2\Omega}, \quad (64)$$

$$\int_{-\infty}^{\infty} \frac{d\nu}{2} \Re \kappa(\nu) = \frac{\pi \langle \Theta^{xx} \rangle}{2T\Omega}. \quad (65)$$

These are known as follows. (a) Equation (64) is the well-known lattice plasma or f-sum rule [44] with the RHS equalling $\omega_p^2/8$ with ω_p as the effective plasma frequency. (b) Equation (65) is the thermal sumrule [37] found recently. From our earlier discussion, we see that the thermal conductivity has a correction for mobile carriers

(equation (17)), so that we can define a finite frequency object

$$\kappa_{zc}(\omega) = \frac{1}{T} \left[L_{22}(\omega) - \frac{L_{12}(\omega)^2}{L_{11}(\omega)} \right], \quad (66)$$

which also satisfies causality and falls off at high frequencies as inverse ω , and therefore satisfies dispersion relations of the type equation (62). Thus by the same argument, and using the high frequency limits of all the coefficients (equation (60)), we infer a sum rule for this case as

$$\int_{-\infty}^{\infty} \frac{d\nu}{\pi} \Re \kappa_{zc}(\nu) = \frac{1}{T\Omega} \left[\langle \Theta^{xx} \rangle - \frac{\langle \Phi^{xx} \rangle^2}{\langle \tau^{xx} \rangle} \right]. \quad (67)$$

The second term in equation (67) is usually small for Fermi systems at low temperatures and usually can be neglected. We may write the RHS as $\pi C_N(T) v_{\text{eff}}^2 / (2d\Omega)$, in terms of the more conventional specific heat for a fixed number of particles and v_{eff} which is defined by this expression. It is interesting to note¹³ that the explicit dependence on the chemical potential in the RHS of equation (65) arising from the definition of \hat{J}_x^Q in equation (34), is exactly cancelled in the RHS of equation (67). Thus the zero current sum rule can be computed without knowing the chemical potential exactly. For immobile carriers this problem is irrelevant; equation (65) can be used without worrying about the distinction between the heat current and energy current.

We should mention that the f-sumrule (equation (64)) and the thermal sum rule (equations (65) and (67)) are both non-universal in a general system and depend upon various material parameters and the temperature. The f-sumrule equals $\omega_p^2/8$ for quadratic bands $\varepsilon_k = \hbar^2 k^2 / (2m)$, but in a tight binding model is related to the kinetic energy expectation. The thermal sumrule is manifestly non-universal since the operators Θ^{xx} explicitly depend on the details of the Hamiltonian [37].

3.7. Dispersion relations for thermopower, Lorentz number and figure of merit

Let us now turn to the main objects of study here, namely,

$$\text{thermopower } S(\omega) = \frac{L_{12}(\omega)}{T L_{11}(\omega)},$$

$$\text{Lorentz number } L(\omega) = \frac{\kappa_{zc}(\omega)}{T \sigma(\omega)},$$

$$\text{figure of merit } Z(\omega)T = \frac{S^2(\omega)}{L(\omega)}. \quad (68)$$

The first two objects are very well known in transport theories [9, 10, 26], while the figure of merit ZT is a dimensionless measure of the efficacy of a thermoelectric device, with large values $ZT \sim 1$ at low T being regarded as highly desirable in many applications. Let us analyse these definitions and extract their dispersion relations. It is readily seen that these variables differ qualitatively from the conductivity or the thermal conductivity in their high frequency behaviour. Each

¹³ I thank Dr S Mukerjee and Dr M Peterson for interesting discussions on this point.

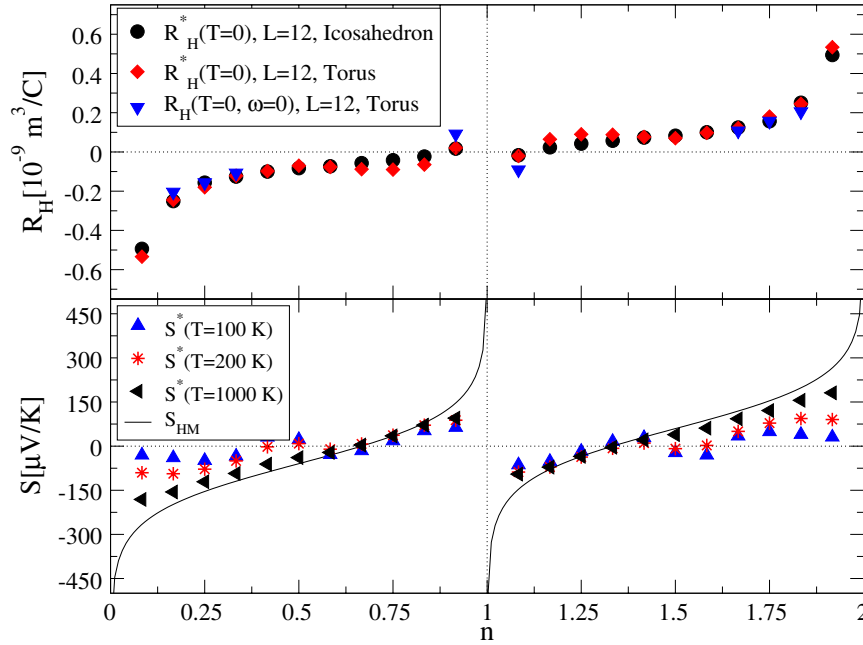


Figure 3. In a Mott–Hubbard system both the Hall constant and the Seebeck coefficient have *three* zero crossings as the band is populated from $0 \leq n \leq 2$. The divergence at half filling is weaker in the Seebeck coefficient than in the Hall constant, as shown in this example from the t – J model on the triangular lattice [29, 35]. The three zero crossings are in contrast to a single zero crossing of an uncorrelated band. The distinction is understood as a consequence of the Mott insulating state at half filling [25, 37]. This insulating state determines the physics of the carriers in its proximity, and these are argued here to be far from the Bloch–Boltzmann holes of standard transport theory. The location of the zero crossings is determined by details such as the lattice structure. Reprinted with permission from [35]a. Copyright 2006 by the American Physical Society.

of these approaches a constant asymptotically, which can be written down by inspection.

$$\text{High freq thermopower } S^* = \frac{\langle \Phi^{xx} \rangle}{T \langle \tau^{xx} \rangle}.$$

$$\text{High freq Lorentz number } L^* = \frac{\langle \Theta^{xx} \rangle}{T^2 \langle \tau^{xx} \rangle} - (S^*)^2.$$

$$\text{High freq figure of merit } Z^* T = \frac{\langle \Phi^{xx} \rangle^2}{\langle \Theta^{xx} \rangle \langle \tau^{xx} \rangle - \langle \Phi^{xx} \rangle^2}. \quad (69)$$

As a result, we can write their dispersion relations readily; they are

$$\Re S(\omega) = S^* + \frac{\mathcal{P}}{\pi} \int_{-\infty}^{\infty} \frac{dv}{v - \omega} \Im m S(v), \quad (70)$$

$$\Re L(\omega) = L^* + \frac{\mathcal{P}}{\pi} \int_{-\infty}^{\infty} \frac{dv}{v - \omega} \Im m L(v), \quad (71)$$

$$\Re Z(\omega) = Z^* + \frac{\mathcal{P}}{\pi} \int_{-\infty}^{\infty} \frac{dv}{v - \omega} \Im m Z(v). \quad (72)$$

These transport quantities are generally real at only two values of frequency, namely zero or infinity, and are very similar in mathematical structure to the Hall resistivity discussed in equation (11). The imaginary part is expected to go linearly at small ω , falling off over some finite interval in ω corresponding to the energy range of the contributing physical processes. Thus the difference between the dc transport and high frequency values can be expressed in all these cases as an

integral over the imaginary part of these three variables divided by the frequency and may be amenable to direct measurements, as in the case of the Hall effect.

4. Thermoelectric phenomena in correlated matter

4.1. Limiting case of free electrons, S^* the Heikes–Mott and Mott results

We propose the use of the high frequency variables (equation (69)) in correlated matter, for reasons that are essentially the same as those for proposing the high frequency Hall constant, explained earlier. These variables are singled out by the fact that they have a finite limit at high ω , as compared with say $\kappa(\omega)$ or $L_{12}(\omega)$, which vanish in that limit. In particular, we expect that these high frequency limits of the three variables listed in equation (69) are good indicators of the dc transport measurements in correlated matter, where we can use the projected t – J model, whereas for the Hubbard model, these should be good only for intermediate to weak coupling. The origin of this expectation is not repeated here since it is identical to the argument given for the Hall constant after equation (9) and the later paragraphs. In the following, we will see the consequences of this proposal and estimate its accuracy in some well-controlled examples. By way of motivating this calculation, we show in figure 3 the computed Hall and Seebeck coefficients for the triangular lattice, where these objects have similar behaviour to a function of electron filling in a Mott–Hubbard system.

Let us begin by listing the three basic operators for the simplest Drude–Sommerfeld type model of a free electron gas, with particle scattering off some impurities or phonons characterized by a relaxation time τ . Let the particle energy dispersion be denoted by ε_k and their group velocity $v_p^x = \partial\varepsilon_k/\partial k_x$. A small calculation of equation (49) shows

$$\begin{aligned}\tau^{xx} &= q_e^2 \sum_{p,\sigma} \frac{\partial}{\partial p_x} \{v_p^x\} c_{p,\sigma}^\dagger c_{p,\sigma}, \\ \Theta^{xx} &= \sum_{p,\sigma} \frac{\partial}{\partial p_x} \{v_p^x(\varepsilon_p - \mu)^2\} c_{p,\sigma}^\dagger c_{p,\sigma}, \\ \Phi^{xx} &= q_e \sum_{p,\sigma} \frac{\partial}{\partial p_x} \{v_p^x(\varepsilon_p - \mu)\} c_{p,\sigma}^\dagger c_{p,\sigma}.\end{aligned}\quad (73)$$

We next form the thermal averages,

$$\begin{aligned}\langle \tau^{xx} \rangle &= 2q_e^2 \sum_p n_p \frac{d}{dp_x} [v_p^x], \\ \langle \Theta^{xx} \rangle &= 2 \sum_p n_p \frac{d}{dp_x} [v_p^x(\varepsilon_p - \mu)^2], \\ \langle \Phi^{xx} \rangle &= 2q_e \sum_p n_p \frac{d}{dp_x} [v_p^x(\varepsilon_p - \mu)].\end{aligned}\quad (74)$$

Here n_p is the Fermi function. We now focus on the low T behaviour of these formulae. At low temperatures T , we use the Sommerfeld expansion [9] after integrating by parts and obtain the leading behaviour:

$$\begin{aligned}\langle \tau^{xx} \rangle &= \Omega 2 q_e^2 \rho_0(\mu) \langle (v_p^x)^2 \rangle_\mu, \\ \langle \Theta^{xx} \rangle &= \Omega T^2 \frac{2\pi^2 k_B^2}{3} \rho_0(\mu) \langle (v_p^x)^2 \rangle_\mu, \\ \langle \Phi^{xx} \rangle &= \Omega T^2 \frac{2q_e \pi^2 k_B^2}{3} \\ &\times \left[\rho_0'(\mu) \langle (v_p^x)^2 \rangle_\mu + \rho_0(\mu) \frac{d}{d\mu} \langle (v_p^x)^2 \rangle_\mu \right],\end{aligned}\quad (75)$$

where $\rho_0(\mu)$ is the density of states per spin per site at the Fermi level μ and the primes denote derivatives w.r.t. μ , the average is over the Fermi surface as usual. We may form high frequency ratios as in equation (69) and get the leading formulae¹⁴

$$S^* = T \frac{\pi^2 k_B^2}{3q_e} \frac{d}{d\mu} \ln[\rho_0(\mu) \langle (v_p^x)^2 \rangle_\mu], \quad (76)$$

$$L^* = \frac{\pi^2 k_B^2}{3q_e^2}. \quad (77)$$

These formulae are indeed very close to what we expect from the Bloch–Boltzmann theory. The high frequency result gives *the same* Lorentz number as we get from the Bloch–Boltzmann theory. In the Bloch–Boltzmann theory, the thermopower can be calculated assuming an energy momentum dependent relaxation time $\tau(p, \omega)$, as

$$S_{\text{Mott}} = T \frac{\pi^2 k_B^2}{3q_e} \frac{d}{d\mu} \ln[\rho_0(\mu) \langle (v_p^x)^2 \tau(p, \mu) \rangle_\mu], \quad (78)$$

¹⁴ The reader is requested to ignore the irksome issue of the dimensionality of the argument of the logarithm. The logarithm is just a notational device to collect the coefficients in this formula and in equations (78) and (88).

and is referred to as the Mott formula [9, 26]. A comparison between the two formulae (equations (76) and (78)) for the thermopower reveals the nature of the high frequency limit: it ignores the energy dependence of the relaxation time, but captures the density of states. Thus this formalism is expected to be accurate whenever the scattering is less important than say the density of states and correlations.

If the free electron gas in the above discussion is replaced by electrons that interact with each other, in addition to scattering off impurities or phonons or amongst themselves, the details of the interactions become crucial in writing down the operators analogous to equation (73). The thermal operators Θ^{xx} can be computed for any given model by a prescription set out in [37], and detailed expressions are available there for many standard electronic models: the Hubbard model, the t – J model and the Anderson model. Also corresponding expressions are available for heat conduction in insulators such as the Heisenberg antiferromagnet and for non-linear lattice models such as the Fermi–Pasta–Ulam chain [45]. The thermoelectric operators Φ^{xx} are also given explicitly for the conducting models for the same set of models in the same reference. Given their length it seems hardly worthwhile to reproduce them here. We merely mention that the operators involve the interaction parameters, just as the energy currents do, and have to be worked out for each model individually. The one exception is the τ^{xx} operator, which usually has the same form as in equation (73), due to the fact that interactions are velocity independent. We will see the explicit form of the Φ^{xx} operator for the $U = \infty$ Hubbard model in equation (92).

Let us also note the general formula for the thermopower from equations (68) and (58). On dropping the second term in equation (59), we get the standard formulae appropriate for dissipative systems, where we can write the ‘exact’ Kubo formula [41]:

$$\begin{aligned}S_{\text{Kubo}} &= \left[\frac{\int_0^\infty dt \int_0^\beta d\tau \langle \hat{J}_x^E(t - i\tau) \hat{J}_x(0) \rangle}{\int_0^\infty dt \int_0^\beta d\tau \langle \hat{J}_x(t - i\tau) \hat{J}_x(0) \rangle} - \frac{\mu(0)}{q_e} \right] \\ &+ \frac{\mu(0) - \mu(T)}{q_e}.\end{aligned}\quad (79)$$

We have used equation (33) and further added and subtracted the $(\mu(0)/q_e)$ term for convenience to arrive at equation (79). The Mott result (equation (78)) follows from this general formula in the limit of weak scattering, as textbooks indicate [10]. For narrow band systems, Heikes introduced another approximation popularized by Mott [46, 47], namely, the Heikes–Mott formula

$$S_{\text{HM}} = \frac{\mu(0) - \mu(T)}{q_e}. \quad (80)$$

This formula emphasizes the thermodynamic interpretation of the thermopower; this term can be loosely regarded as the entropy per particle¹⁵. This motivates us [37] to decompose the thermopower as

$$S_{\text{Kubo}} = S_{\text{Tr}} + S_{\text{HM}}, \quad (81)$$

¹⁵ Strictly speaking μ is a derivative of the entropy w.r.t. the number of particles, i.e. $\mu(T) = -T(\partial S(N, T)/\partial N)_{E, T}$.

thereby defining the ‘transport part’ of thermopower as the first part of equation (79) evaluated with $\mu(0)$, as opposed to the thermodynamic part S_{HM} . Using the high frequency approximation (equation (69)), we approximate (only) the transport part in equation (81) and write

$$S^* = S_{\text{Tr}}^* + S_{\text{HM}},$$

$$S_{\text{Tr}}^* = \frac{\langle \Phi^{xx} \rangle}{T \langle \tau^{xx} \rangle}, \quad (82)$$

with the Φ^{xx} differing from the variable Φ^{xx} in that the chemical potential μ is replaced by the $T = 0$ value $\mu(0)$. The low T limit for the free particle case of this relation is given in equation (76). For a correlated many body system, it is much easier to work with this variable. The computational advantage in equation (82) over equation (79) is that the transport part is approximated by an equal time correlator as opposed to a dynamical correlator. This allows us to apply one of several possible techniques to the problem, such as exact diagonalization and also high T expansions.

4.2. Kelvin’s thermodynamical formula for thermopower

It is interesting to discuss Kelvin’s thermodynamic derivation of the thermopower [40]. In his seminal work, Onsager [38] discussed Kelvin’s derivation of reciprocity given several decades earlier. He argued that the phenomenon of transport, including reciprocity, cannot be understood within equilibrium thermodynamics or statistical mechanics. Interestingly as late as 1966, Wannier wrote in his textbook [48]: ‘*Opinions are divided as to whether Kelvin’s derivation is fundamentally flawed or not*’. A detailed account of this debate and its resolution seem to be missing in the literature.

Our discussion on the thermopower takes us to the brink of this old debate, and so we make a small excursion to obtain a thermodynamic approximation of the correct answer. This derivation captures the spirit of the Kelvin argument and provides an approximate expression for the thermopower S . For deriving this, let us rewind to equation (43) of the finite q , ω dependent Onsager coefficients $L_{ij}(q, \omega)$. Using equations (39), (41) and (42) we see that

$$L_{11}(q, \omega) = \frac{i}{\Omega q_x} \chi_{\hat{J}_x(q_x), \rho(-q_x)}(\omega),$$

$$L_{12}(q, \omega) = \frac{i}{\Omega q_x} \chi_{\hat{J}_x(q_x), K(-q_x)}(\omega),$$

hence

$$S(q_x, \omega) = \frac{\chi_{\hat{J}_x(q_x), K(-q_x)}(\omega)}{T \chi_{\hat{J}_x(q_x), \rho(-q_x)}(\omega)}. \quad (83)$$

Onsager’s prescription at this point is to take the transport limit, i.e. first let $q_x \rightarrow 0$ followed by the static limit, to get the exact formula [39, 41]. We saw in the previous section that this ratio has another finite and interesting limit, leading to S^* , when we let $q_x \rightarrow 0$ followed by $\omega \gg 0$. It is interesting and amusing that in the opposite slow limit, i.e. $\omega \rightarrow 0$ followed by $q_x \rightarrow 0$, once again $S(q_x, \omega)$ has a finite and well-defined result. This limit is what we identify with the Kelvin calculation and his

formula, since the objects that arise are purely equilibrium quantities. Thus

$$S_{\text{Kelvin}} = \lim_{q_x \rightarrow 0, \omega \rightarrow 0} S(q_x, \omega),$$

$$S(q_x, \omega) = \frac{\chi_{[K, \rho(q_x)], K(-q_x)}(\omega)}{T \chi_{[K, \rho(q_x)], \rho(-q_x)}(\omega)} \quad (84)$$

$$= \frac{\chi_{\rho(q_x), K(-q_x)}(\omega)}{T \chi_{\rho(q_x), \rho(-q_x)}(\omega)}. \quad (85)$$

We have used the continuity relation $\hat{J}_x(q_x) = (1/q_x)[K, \rho(q_x)]$ to go from equation (83) to equation (84). The next stage involves writing a Ward type identity,

$$\chi_{[K, \rho(q_x)], K(-q_x)}(\omega) = -\omega \chi_{\rho(q_x), K(-q_x)}(\omega) + [K(-q_x), \rho(q_x)], \quad (86)$$

and a similar one for the denominator, followed by realizing that the second term of the r.h.s. of equation (86) vanishes on using parity for any finite q in a system with inversion symmetry¹⁶. We can now take the static limit and get the equilibrium Kelvin result

$$S_{\text{Kelvin}} = \lim_{q_x \rightarrow 0} \frac{\chi_{\rho(q_x), K(-q_x)}(0)}{T \chi_{\rho(q_x), \rho(-q_x)}(0)}, \quad (87)$$

where in the limit, the denominator is related to the thermodynamic compressibility, and the numerator is an equilibrium cross correlation function between energy and charge density. It is straightforward to see that reciprocity holds in this sequence of limits as well.

In the case of free particles, it is easy to evaluate equation (87) at low T and we find

$$S_{\text{Kelvin}} = T \frac{\pi^2 k_B^2}{3q_e} \frac{d}{d\mu} \ln[\rho_0(\mu)]. \quad (88)$$

It is amusing to compare equations (76) and (78) and equation (88). Compared with the ‘exact’ Mott formula that follows from the Onsager limiting procedure, S^* captures the answer except for the energy dependent relaxation rate. The Kelvin formula further approximates S^* by neglecting the energy dependence of the velocity average. Thus we conclude that the Kelvin approximation is inferior to the high frequency approximation, but does capture the density of states effects.

The above rather formal manipulation with the limits can be nicely visualized by working instead with open boundary conditions. Let us imagine a ‘gedanken experiment’, where a long isolated cylinder of the material of interest, with length L , is subjected to a time varying temperature gradient. Since this experiment is exempt from practical issues, we further imagine a Luttinger version of this, where a pair of tiny blackholes¹⁷ are brought to the two ends of the sample

¹⁶ The argument is trivial for the denominator since density fluctuations commute at different wave vectors. In the numerator, consider the real expectation $\gamma(q_x) = \langle [K(-q_x), \rho(q_x)] \rangle$. Clearly $\gamma^*(q_x) = \langle [\rho(-q_x), K(q_x)] \rangle = -\gamma(-q_x)$. But from parity $\gamma(-q_x) = \gamma(q_x)$ and hence the result $\gamma(q_x) = 0$.

¹⁷ If the earth became a black hole it would have a diameter of about 0.017m, about the size of a marble. http://www.windows.ucar.edu/tour/link=kids_space/black.html&edu=elem.

(somehow!!) and oscillated in space and time. Thus we apply a space–time varying gravitational field $\psi(\vec{x}, t) = \delta\psi_0(x/L)\exp\{-i\omega t\}$ together with a similar electrostatic potential $\phi(\vec{x}, t)$ and compute the induced oscillating dipole moment $P = \sum_x x\rho(\vec{x})$ using perturbation theory. The gravitational field is again a proxy for temperature variation. By forming the ratio of the gravitational field amplitude $\delta\psi_0$ to the electrostatic amplitude $\delta\phi_0$ needed to produce a given dipole moment, we can extract the thermopower. The rigorously correct transport limit, as applied to this situation, requires *the thermodynamic limit to be taken before* $\omega \rightarrow 0$. If we compute the opposite limit instead, i.e. a finite system and a dc field, then the result maps to equation (87). Such a limiting process is tempting from the physical picture of the so-called ‘absolute thermopower’. In this case, one studies a single system with applied thermal gradients, which develops a voltage across its ends. This type of a picture was presumably behind the Kelvin derivation.

4.3. Applications to sodium cobaltates in the Curie–Weiss metallic phase

At this point it is worthwhile to compare the results of various approximations in the important and current problem of sodium cobaltates Na_xCoO_2 , with $x \sim 0.68$. Recent interest in this system started with the observation of high thermopower ($S \sim 80 \mu\text{V K}^{-1}$) at room temperatures in this system by Terasaki [18]. Wang, Rogado, Cava and Ong, in another important paper [19], found that this thermopower is strongly magnetic field dependent. They further found that the metallic conduction is coexistent with a Curie–Weiss susceptibility characteristic of insulators. This has given rise to the nomenclature of a Curie–Weiss metallic phase. The basic modelling of this system, as suggested by Wang *et al* is in terms of a strongly correlated Fermi system, with no double occupancy of holes. The holes move on a triangular lattice provided by the Co atoms, and the system may be regarded, to a first approximation, as a bunch of uncoupled 2D triangular lattice planes with a t – J model description of correlated holes. After performing a particle hole transformation we can write the basic Hamiltonian as

$$H = - \sum_{\vec{x}, \vec{\eta}} t(\vec{\eta}) \tilde{c}_{\vec{x}+\vec{\eta}, \sigma}^\dagger \tilde{c}_{\vec{x}, \sigma} + J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j. \quad (89)$$

Here $\vec{\eta}$ is the nearest neighbor vector on the triangular lattice.

This model corresponds to the limit of $U \rightarrow \infty$. In this limit the Fermionic commutation relations need to be modified into the Gutzwiller–Hubbard projected operator [49] relations (with $\vec{\sigma} = -\sigma$):

$$\begin{aligned} \tilde{c}_{\vec{x}, \sigma} &= P_G c_{\vec{x}, \sigma} P_G, \\ \{\tilde{c}_{\vec{x}, \sigma}, \tilde{c}_{\vec{x}', \sigma'}^\dagger\} &= \delta_{\vec{x}, \vec{x}'} \{\delta_{\sigma, \sigma'} (1 - n_{\vec{x}, \vec{\sigma}}) + (1 - \delta_{\sigma, \sigma'}) \tilde{c}_{\vec{x}, \sigma}^\dagger \tilde{c}_{\vec{x}, \sigma}\} \\ &\equiv Y_{\sigma, \sigma'} \delta_{\vec{x}, \vec{x}'}. \end{aligned} \quad (90)$$

The presence of the Y factor is due to strong correlations and makes the computation non-trivial. The number operator $n_{\vec{x}, \sigma}$ is unaffected by the projection. Let us consider the kinetic energy only, i.e. the t part, since this is expected to dominate

in transport properties, at least far enough from half filling and for $t \gg J$. The addition of the J part can be done without too much difficulty; in fact, the numerics discussed below include the full Hamiltonian.

Let us note down the expressions for the charge current and the energy current at finite wave vectors by direct computation:

$$\hat{K}(k) = - \sum_{\vec{x}, \vec{\eta}, \sigma} (t(\vec{\eta}) + \mu \delta_{\vec{\eta}, 0}) e^{i\vec{k} \cdot (\vec{x} + \frac{1}{2}\vec{\eta})} \tilde{c}_{\vec{x}+\vec{\eta}, \sigma}^\dagger \tilde{c}_{\vec{x}, \sigma}, \quad (91)$$

$$\hat{J}_x(k) = iq_e \sum_{\vec{x}, \vec{\eta}, \sigma} \eta_x t(\vec{\eta}) e^{i\vec{k} \cdot (\vec{x} + \frac{1}{2}\vec{\eta})} \tilde{c}_{\vec{x}+\vec{\eta}, \sigma}^\dagger \tilde{c}_{\vec{x}, \sigma},$$

$$\begin{aligned} \hat{J}_x^Q(k) &= -\frac{i}{2} \sum_{\vec{x}, \vec{\eta}, \vec{\eta}', \sigma} (\eta_x + \eta'_x) t(\vec{\eta}) t(\vec{\eta}') \\ &\times e^{i\vec{k} \cdot (\vec{x} + \frac{1}{2}(\vec{\eta} + \vec{\eta}'))} Y_{\sigma', \sigma}(\vec{x} + \vec{\eta}') \tilde{c}_{\vec{x}+\vec{\eta}+\vec{\eta}', \sigma}^\dagger \tilde{c}_{\vec{x}, \sigma} - \frac{\mu}{q_e} \hat{J}_x(k). \end{aligned}$$

We evaluate the thermoelectric operator as

$$\begin{aligned} \Phi^{xx} &= -\frac{q_e}{2} \sum_{\vec{\eta}, \vec{\eta}', \vec{\sigma}, \vec{x}} (\eta_x + \eta'_x)^2 t(\vec{\eta}) t(\vec{\eta}') Y_{\sigma', \sigma} \\ &\times (\vec{x} + \vec{\eta}) \tilde{c}_{\vec{x}+\vec{\eta}+\vec{\eta}', \sigma}^\dagger \tilde{c}_{\vec{x}, \sigma} - q_e \mu \sum_{\vec{\eta}, \sigma, \vec{x}} \eta_x^2 t(\vec{\eta}) \tilde{c}_{\vec{x}+\vec{\eta}, \sigma}^\dagger \tilde{c}_{\vec{x}, \sigma}. \end{aligned} \quad (92)$$

This expression gives an idea of the complexity of the operators that arise in the theory. Let us first present some numerical results obtained by exact diagonalization [50, 51] of small clusters of the triangular lattice. We can compute all eigenstates and matrix elements for up to 14 or 15 site clusters of the triangular lattice. We can therefore assemble the full dynamical conductivities from equation (68). The involved calculations are fully described in the papers [50, 51], and we will content ourselves with displaying the main results. Firstly, consider the absolute scale of the thermopower S^* as a function of temperature, shown in figure 4. The upper panel in figure 4 shows that this comparison with experiment is quite successful on a quantitative scale. One can next ask; how good is the approximation of infinite frequency, purely in theoretical terms. To answer this we compute the frequency dependence of $S(\omega)$, as shown in figure 5. It is clear from this figure that the approximation of high frequency is excellent, the maximum error being less than 3%. Thus we are computing essentially the dc transport object, at least for clusters of these sizes. This benchmarking gives us confidence in the results of the high frequency formulae for thermopower.

4.4. High temperature expansion for thermopower

We next show that rather simple considerations of our formulae lead to an important prediction for enhancing the thermopower for a triangular lattice system with a suitable choice of the hopping parameter. We find a remarkable effect of the sign of hopping on the transport part of the thermopower. This is well illustrated in the lower panel of figure 4. This shows the enhancement of the computed thermopower at low and intermediate T s, achieved by flipping the sign of hopping from the upper panel. We perform a simple computation at high T that throws light on this phenomenon. We focus on the

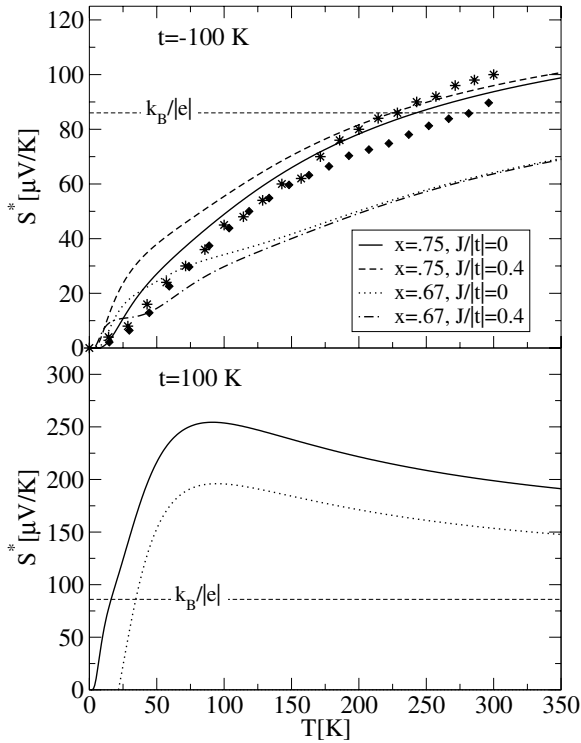


Figure 4. Upper panel: thermopower computed for the triangular lattice t - J model in [35], compared with the experimental data of [18] (stars) and [19] (diamonds). The absolute scale is set by a single parameter $t = -100$ K. The different curves correspond to various values of doping x and $J/|t|$. Lower panel: this shows the effect of reversing the sign of hopping in this system. This is a prediction of this theory for a fiduciary hole doped sodium cobaltate type system. The peak value of $250 \mu\text{V K}^{-1}$ can be further manipulated upwards by changing material parameters J, x .

$$x=0.67, t>0, J=0.2|t|$$

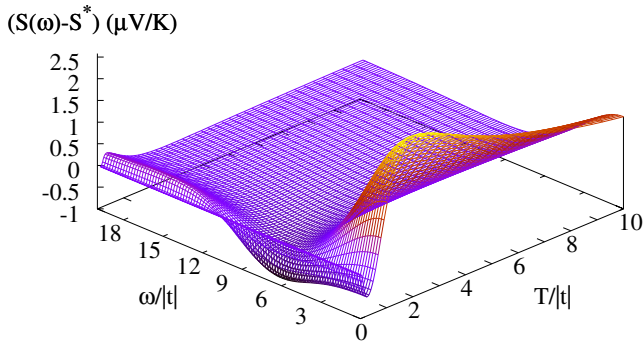


Figure 5. The frequency dependence of the thermopower computed for the triangular lattice t - J model from [51]. The sign of hopping is flipped relative to that in figure (4) in this and all other figures by using a p-h mapping. Recalling that the scale of $S \sim 100 \mu\text{V K}^{-1}$, we conclude that the frequency dependence is indeed very small ($\sim 3\%$ at most). Reprinted with permission from [51]. Copyright 2007 by the American Physical Society.

kinetic energy which is expected to dominate the transport contributions. Let us compute the thermopower S^* from equations (69) and (92)

$$S^* = -\frac{\mu}{q_e T} + \frac{q_e \Delta}{T \langle \tau^{xx} \rangle}, \quad (93)$$

where

$$\Delta = -\frac{1}{2} \sum_{\vec{\eta}, \vec{\eta}', \vec{x}} (\eta_x + \eta'_x)^2 t(\vec{\eta}) t(\vec{\eta}') \langle Y_{\sigma', \sigma}(\vec{x} + \vec{\eta}) \tilde{c}_{\vec{x} + \vec{\eta} + \vec{\eta}', \sigma'}^\dagger \tilde{c}_{\vec{x}, \sigma} \rangle. \quad (94)$$

The computation of the different parts proceeds as follows: we show readily that (for the hole doped case) using translation invariance and with n as the number of particles per site at high T ,

$$\langle \tau^{xx} \rangle = 6\Omega q_e^2 t \langle \tilde{c}_1^\dagger \tilde{c}_0 \rangle \sim 3\Omega q_e^2 \beta t^2 n(1-n). \quad (95)$$

The structure of the term equation (94) is most instructive. At high temperatures, for a square lattice we need to go to second order in βt to get a contribution with $\eta_x + \eta'_x \neq 0$ to the expectation of the hopping $\langle \tilde{c}_{\vec{x} + \vec{\eta} + \vec{\eta}', \sigma'}^\dagger \tilde{c}_{\vec{x}, \sigma} \rangle$. For the triangular lattice, on the other hand, we already have a contribution at first order. For the triangular lattice, corresponding to each nearest neighbor, there are precisely two neighbors where the third hop is a nearest neighbor hop. A short calculation gives

$$\Delta \sim -3\Omega t^2 \sum_{\sigma, \sigma'} \langle Y_{\sigma', \sigma}(\vec{\eta}) \tilde{c}_{\vec{\eta} + \vec{\eta}', \sigma'}^\dagger \tilde{c}_{\vec{0}, \sigma} \rangle. \quad (96)$$

The spins must be the same to the leading order in βt where we generate a hopping term $\tilde{c}_{\vec{0}, \sigma}^\dagger \tilde{c}_{\vec{\eta} + \vec{\eta}', \sigma}$ from an expansion of $\exp(-\beta K)$, and hence a simple estimation yields

$$\Delta = -\frac{3}{2}\Omega t^3 \beta n(1-n)(2-n) + O(\beta^3). \quad (97)$$

This together with $\mu/k_B T = \log(n/2(1-n)) + O(\beta^2 t^2)$ gives us the result for $0 \leq n \leq 1$

$$S^* = \frac{k_B}{q_e} \left\{ \log[2(1-n)/n] - \beta t \frac{2-n}{2} + O(\beta^2 t^2) \right\}, \quad (98)$$

and

$$S^* = -\frac{k_B}{q_e} \left\{ \log[2(n-1)/(2-n)] + \beta t \frac{n}{2} + O(\beta^2 t^2) \right\} \quad (99)$$

for $1 \leq n \leq 2$ using particle hole symmetry [37].

We observe that the first term in equation (93) from $\mu(T)$ arising from thermodynamics, termed the Heikes–Mott contribution, dominates at very high T . The approach to this value is governed by the second term of equation (93), called the transport term. This transport term is $O(\beta t)$ for the triangular lattice, whereas it is only $O(\beta t)^2$ for the square lattice due to the existence of closed loops of length three in the former. The high T expansion clearly identifies the role of the lattice topology here. The other important consequence is the dependence upon the sign of the hopping in the transport term. To be specific, for electron doping the thermopower in equation (99) shows that S approaches its high T limit from below as long as $t < 0$, as we find for sodium cobaltates [18, 19]. On the other hand, if we could flip the sign of the hopping, as in a fiduciary hole doped cobalt oxide layer, the high T value would be reached from above. Since the S must vanish at low T , this observation implies that we must find a maximum in $S(T)$ at some intermediate T . This then motivates the calculation for a fiduciary system with the flipped sign of hopping. As seen in figures 4, and 6, numerical

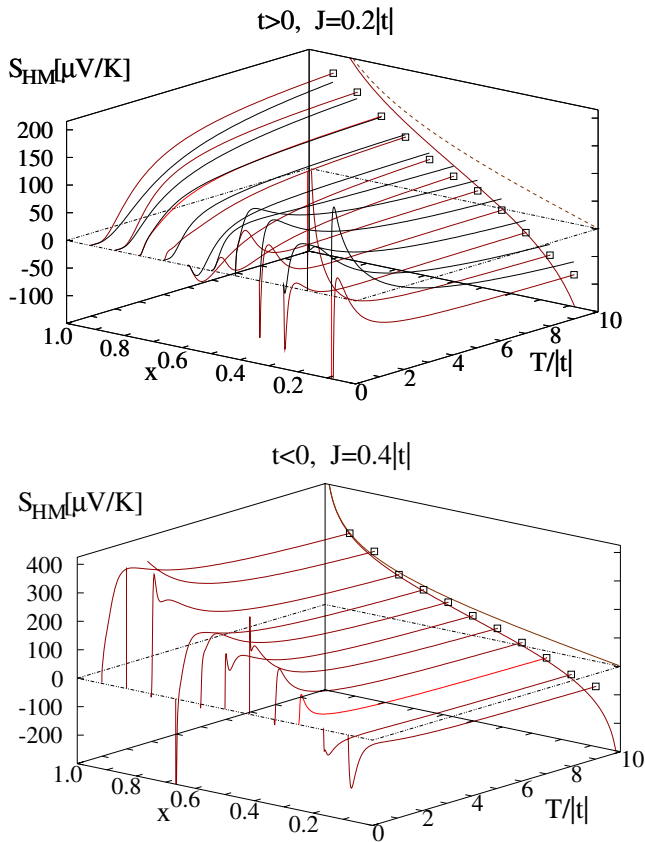


Figure 6. The thermopower versus filling $x = 1 - n$ and temperature T in the t - J model from numerical studies [50, 51] on clusters of the triangular lattice. In both cases the lower curves correspond to the Heikes–Mott formula (equation (80)) and the upper to the high frequency result of equation (69). Left: the case of the sodium cobaltates, i.e. electron doping, where the two estimates are very close. Right: the fiduciary hole doped cobaltate. The two curves in the high T limit correspond to the first term in equation (98) and from the uncorrelated chemical potential. For the case on right, the Heikes–Mott formula misses the enhancement that the high frequency formula predicts. Such enhanced values of the thermopower are very exciting in the current quest for better materials. Reprinted with permission from [51]. Copyright 2007 by the American Physical Society.

results are very encouraging, leading to a thermopower that is $\sim 250 \mu\text{V K}^{-1}$ and should act as an incentive to the materials community who could seek this type of doping. Crystal structures containing triangular loops are clearly favourable, and this includes several 3D structures as well, such as the FCC and HCP lattices.

4.5. Lorentz number and figure of merit for the triangular lattice t - J model

We briefly indicate the dependence of the Lorentz number L^* and the figure of merit Z^*T as computed by us in the case of the triangular lattice [50, 51], with parameters appropriate for sodium cobaltates at $x \sim 0.68$. Figure 7 indicates the dependence of these important parameters on x , T for the t - J model clusters of size up to 14. The frequency dependence was estimated to be small and of the same scale as that of $S(\omega)$, and therefore the results are good indicators of the dc

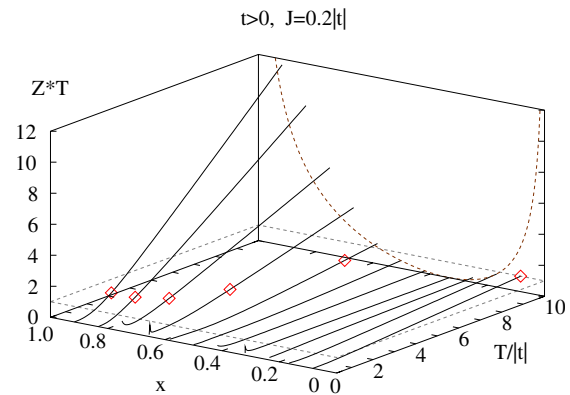


Figure 7. Left: the dimensionless figure of merit Z^*T versus x , T for the same system from [51]. This is purely an electronic value of the power factor, the phonon contribution to κ is expected to be significant and would clearly make the situation less ‘ideal’, thereby we expect the true Z^*T to be considerably decreased. However, this figure gives an overview of the purely electronic contribution to the figure of merit for parameters roughly comparable to those in $\text{Na}_{0.7}\text{CoO}_2$. The conclusion in this case is that proximity to half filling is not particularly useful. A similar plot for the fiduciary case of the flipped sign of hopping gives a considerably larger value of the figure of merit. Reprinted with permission from [51]. Copyright 2007 by the American Physical Society.

values. We must keep in mind that the finite size effects are substantial for these small clusters, and hence the behaviour at low T is particularly subject to corrections. Also we stress that our calculation pertains to the electronic part of the thermal conduction and neglects the often substantial lattice part. Our figure of merit is therefore likely to be a rather optimistic upper bound to the physical values. Correcting for the lattice part using measured thermal conductivity is straightforward in specific cases. More non-trivially, an elaborate topic treated in a recent work deals with manipulating the lattice part to maximize the figure of merit by suitably chosen lattice structures and impurities [52]. However, it is clear that several interesting trends emerge from this purely electronic study. A striking trend is that the proximity of the Mott–Hubbard insulating state $x \sim 0$ is not necessarily favourable for good thermoelectric behaviour with a large Z^*T . This is despite the enhancement of S itself. The enhancement arises due to Mott–Hubbard correlations that lead to a logarithmic divergence of S near half filling [35], but is offset by the unfavourable Lorentz ratio. On the other hand, the proximity of almost filled bands or almost empty bands seems to be more favourable, and indeed the experience with doping in Na_xCoO_2 seems to bear out this finding rather well.

5. Phenomenological equations for coupled charge and energy transport

In this section, we present a simple framework for the problem of coupled transport of charge and energy (or heat) in a charged system, such as a semiconductor or a poor metal. It is perturbed by an external temperature gradient and electric fields. We add a source that dumps energy into the system, such as a pump laser, motivated by several recent

experiments [53–58]. In these experiments, a cylindrical rod of a semiconductor (or metal) is subjected to pulsed laser heating at one end¹⁸. The resulting change in the reflectivity of a second probe laser conveniently provides a readout of the local ‘dynamical temperature’ [53–55]. This enables the reconstruction of several physically interesting variables, such as the electron phonon coupling [56], the thermal conductivity [57] and the thermoelectric coefficient [58]. Given the time dependence of the probes, we clearly need ac response functions of the type discussed above. The laser modulation time constants currently are in the femtosecond range (10^{-15} s), and hence are already able to probe energy relaxation times in semiconductors [57]. Such non-trivial observations motivate modelling of the type described below.

Our framework is a simple model of charge and heat diffusion (e.g. [59, 60]) together with the exact coefficients relating the rate of change in currents to the driving forces. The dynamical formalism set out in earlier sections is provided a simple context here and sheds light on the meaning of new operators τ^{xx} , Θ^{xx} , Φ^{xx} constructed above in equation (49). These play a fundamental role here, thereby providing a strong pedagogical motivation for this section, in addition to the above-mentioned practical one. In our simple model, we find it advantageous to define new response functions measuring the change in energy, charge density and the currents arising from the input power (the coefficients M_1 , M_2 , N_1 , N_2 below in equation (108)). These are related to the \bar{q} , ω dependent Onsager coefficients L_{ij} via the various continuity equations and Einstein type relations, but clearly and neatly isolate the ‘force-response’ aspect of the external power probe and as such give a direct method of interpreting experiments.

In essence, we approach this problem through a ‘mechanical perturbation’ point of view rather than a thermodynamic one. Our strategy is to stick to the most broadly definable variables, such as the energy density and currents, and to avoid, or at least postpone until the very end, the mention of variables such as \bar{q} , ω dependent *temperature fluctuations*. The latter are only sensible in the domain of long wavelength and low frequency variations, unlike the former which are always definable. The results for temperature fluctuations emerge usefully from our formulae in the limiting sense at the end of the calculation.

Let us imagine the system in the form of a cylinder of cross section A and length L along the x axis ($\Omega = LA$), with the surface layer at $x = 0$. We subject the system to an external Luttinger field $\psi(\vec{x}, t) = \psi_q \exp -i(\omega t + q_x x)$, an electrostatic potential $\phi(\vec{x}, t) = \phi_q \exp -i(\omega t + q_x x)$. We introduce the pump laser term below via the continuity equation below. Since we will discuss a charged system, it must be stressed that the electric potential satisfies the Poisson equation with the induced charge density included, so that $\vec{E} = -\nabla\phi$ is the *total local electric field*. The system is then described by the Hamiltonian equation (38) We will

¹⁸ This end is usually covered by a surface cap of a good metal, where the absorption of the laser power occurs and is transmitted to the system via a contact layer.

denote the (grand canonical) Hamiltonian in the absence of the perturbing fields as K_0 and the perturbation as K_1 . As usual the quantum average of an observable is given by $\langle Q \rangle = \text{Tr}(Q\hat{\rho}(t))$, where the density matrix $\hat{\rho}$ satisfies the von Neumann equation $i(\partial/\partial t)\hat{\rho}(t) = [K_{\text{tot}}(t), \hat{\rho}(t)]$, and hence any observable expectation satisfies the equation $i(\partial/\partial t)\langle Q(t) \rangle = \langle [Q, K_1] \rangle_0 + \langle [Q, K_0] \rangle$. The first term has been linearized and hence evaluated in the unperturbed ensemble with $K = K_0$, and the second term can be evaluated within perturbation theory as usual, and we find the exact linearized equation of motion:

$$i\frac{\partial}{\partial t}\langle Q(t) \rangle = \langle [Q, K_1] \rangle_0 + (-i) \int_0^\infty dt' e^{i\omega t' - 0^+ t} \langle [[Q(t), K_0], K_1(-t')] \rangle_0. \quad (100)$$

Interestingly enough, the first term in equation (100) is expressible exactly in terms of the three operators in equation (68), while the second term is approximated by a relaxational plus diffusive term. We choose the variables Q as the heat (\hat{J}_x^Q) and charge (\hat{J}_x) currents and the densities of heat K and charge ρ as before. Exploiting the linearity of the theory, it suffices to consider a single frequency and wave vector at the input, and hence we introduce a notation for the induced variables depending on the single wave vector q_x through

$$\begin{aligned} \langle \hat{J}_x^Q(\vec{x}, t) \rangle &= \frac{1}{\Omega} e^{-i\omega t - iq_x x} \delta J_x^Q, \\ \langle \hat{J}_x(\vec{x}, t) \rangle &= \frac{1}{\Omega} e^{-i\omega t - iq_x x} \delta J_x, \\ \langle K(\vec{x}, t) \rangle &= \frac{1}{\Omega} e^{-i\omega t - iq_x x} \delta K_q + \frac{1}{\Omega} \langle K \rangle_0, \\ \langle \rho(\vec{x}, t) \rangle &= \frac{1}{\Omega} e^{-i\omega t - iq_x x} \delta \rho_q + q_e n. \end{aligned} \quad (101)$$

Thus the variables $\langle \hat{J}_x^Q(\vec{x}, t) \rangle$, etc are intensive whereas δJ_x^Q , etc are extensive. Next, the pump laser coupling to the system is introduced via the continuity equation for energy. We write the energy continuity equation (ignoring the variations along the transverse directions and focusing on the x axis variation) as

$$\frac{\partial}{\partial t} \langle K(\vec{x}, t) \rangle + \frac{\partial}{\partial x} \langle \hat{J}_x^Q(\vec{x}, t) \rangle = P_0 \delta(x). \quad (102)$$

We introduced the input power P_0 per unit area at the surface layer $x = 0$ ¹⁹. The power P_0 is further modulated in time, so that we decompose it as $P_0 \exp -i(\omega t)$. We finally note the conservation laws for charge and energy densities in terms of

¹⁹ If we introduce the coupling of the laser field \vec{E}^0 to the matter in K_{tot} , it leads to an operator equation of continuity for energy which contains $\vec{J} \cdot \vec{E}^0$ at the surface. Our treatment roughly corresponds to writing $\vec{J} = \sigma_{\text{sur}} \vec{E}^0$, where σ_{sur} is the conductivity at the surface, and averaging this Joule heating over the time period of the laser $2\pi/\omega_0$. Assume a skin depth l so that the power absorbed per unit area $P_0 = \frac{1}{2} l \sigma_{\text{sur}} |\vec{E}^0|^2$. Depending on the set-up, this might need to be further corrected for a contact (Kaptiza) resistance between the cap and the sample.

the response amplitudes:

$$\begin{aligned} q_x \delta J_x^Q + \omega \delta K_q &= iA P_0, \\ q_x \delta J_x + \omega \delta \rho_q &= 0. \end{aligned} \quad (103)$$

We next note that the first term in the dynamical equation (100) for both the currents is *exactly expressible in terms of the operators defined in equation (49)*. For example, consider the heat current equation where the term in question reads $\langle [\hat{J}_x^Q(q), K(-q)] \rangle_0 \psi_q + \langle [\hat{J}_x^Q(q), \rho(-q)] \rangle_0 \phi_q$. For small q , upon using equation (49) it becomes $-\langle \Theta^{xx} \rangle_0 q \psi_q - \langle \Phi^{xx} \rangle_0 q \phi_q$. Similar expressions hold for the charge current. In the absence of the second term in equation (100), the equations are ballistic, and hence the sum rules discussed earlier are closely related to the behaviour of the response functions in this regime. This little calculation gives us the physical meaning of these operators Θ^{xx}, Φ^{xx} ; *their expectation value determines the magnitude of the ballistic force exerted by the fields*. The second term is, of course, crucial, and we need to estimate it using some general principles. We write the phenomenological equations:

$$\begin{aligned} \left[\frac{1}{\tau} + \frac{d}{dt} \right] \langle \hat{J}_x^Q(\vec{x}, t) \rangle &= -\frac{D_Q}{\tau} \nabla \langle K(\vec{x}t) \rangle - \frac{c_1}{\tau} \nabla \langle \rho(\vec{x}t) \rangle \\ &- \left\{ \frac{\langle \Theta^{xx} \rangle_0}{\Omega} \nabla \psi(\vec{x}t) + \frac{\langle \Phi^{xx} \rangle_0}{\Omega} \nabla \phi(\vec{x}t) \right\} \end{aligned} \quad (104)$$

and

$$\begin{aligned} \left[\frac{1}{\tau} + \frac{d}{dt} \right] \langle \hat{J}_x(\vec{x}, t) \rangle &= -\frac{c_2}{\tau} \nabla \langle K(\vec{x}t) \rangle - \frac{D_c}{\tau} \nabla \langle \rho(\vec{x}t) \rangle \\ &- \left\{ \frac{\langle \tau^{xx} \rangle_0}{\Omega} \nabla \phi(\vec{x}t) + \frac{\langle \Phi^{xx} \rangle_0}{\Omega} \nabla \psi(\vec{x}t) \right\}. \end{aligned} \quad (105)$$

These equations represent the effect of the second term in equation (100) by terms proportional to the gradients of the heat and charge densities and are relaxational and diffusive in nature. D_Q, D_c are the heat and charge diffusion constants, and the cross diffusion terms c_1, c_2 are determined below. The basic physics contained in the diffusion terms is that in steady state (where the time derivatives of the currents are zero), and in the absence of external mechanical fields, one can yet have charge and heat currents driven by gradients of the charge and heat densities. The relaxation time $\tau \equiv \tau(\vec{q}, \omega)$, in general, depends upon \vec{q}, ω and gives the rate at which the currents relax to zero. Within this model τ must necessarily be the same for both charge and energy currents, otherwise the generalized Onsager reciprocity at finite frequencies $L_{12}(\omega) = L_{21}(\omega)$ is violated. Let us also note equation (105) in terms of the induced amplitudes in the Fourier representation:

$$\begin{aligned} (1 - i\omega\tau) \delta J_x^Q &= i\tau \{ \langle \Theta^{xx} \rangle_0 q \psi_q + \langle \Phi^{xx} \rangle_0 q \phi_q \} \\ &+ iD_Q q \delta K_q + ic_1 q \delta \rho_q, \\ (1 - i\omega\tau) \delta J_x &= i\tau \{ \langle \Phi^{xx} \rangle_0 q \psi_q + \langle \tau^{xx} \rangle_0 q \phi_q \} \\ &+ ic_2 q \delta K_q + iD_c q \delta \rho_q. \end{aligned} \quad (106)$$

The constants D_Q, D_c, c_1, c_2 can be fixed by considering the static limit at finite q where the currents and their time derivatives are zero. equating the various coefficients on the right to zero and taking the long wavelength limit, we determine these as follows:

$$\begin{aligned} D_Q &= -\tau \langle \Theta^{xx} \rangle_0 \frac{\psi_q}{\delta K_q} = \tau \frac{\langle \Theta^{xx} \rangle_0}{C(T)T}, \\ D_c &= -\tau \langle \tau^{xx} \rangle_0 \frac{\phi_q}{\delta \rho_q} = \tau \frac{\langle \tau^{xx} \rangle_0}{\Omega} \frac{1}{q_e^2} \frac{d\mu}{dn}, \\ c_1 &= D_c \frac{\langle \Phi^{xx} \rangle_0}{\langle \tau^{xx} \rangle_0}, \quad c_2 = D_Q \frac{\langle \Phi^{xx} \rangle_0}{\langle \Theta^{xx} \rangle_0}. \end{aligned} \quad (107)$$

Here $C(T)$ is the (extensive) specific heat, and $\frac{d\mu}{dn}$ is the compressibility per unit volume. We have made use of the standard thermodynamic definitions of these response functions to arrive at these relations. Thus all parameters are fixed in terms of the averages of the three operators in equation (49), a single relaxation time and the two thermodynamic response functions. For a single frequency mode, these coupled equations together with the conservation laws (equation (103)) can be solved easily and the results expressed as

$$\begin{aligned} \frac{1}{\Omega} \delta J_x^Q &= L_{22}(iq\psi_q) + L_{21}(iq\phi_q) + M_2 \frac{P_0}{L}, \\ \frac{1}{\Omega} \delta J_x &= L_{12}(iq\psi_q) + L_{11}(iq\phi_q) + M_1 \frac{P_0}{L}. \end{aligned} \quad (108)$$

In addition to the standard Onsager coefficients L_{ij} , we have defined the power response functions M_j as above, giving the response of the currents to P_0 . It is also interesting to define the response of the charge and energy density to the applied power P_0 via

$$N_1 = \frac{1}{A} \frac{\partial \delta \rho_q}{\partial P_0}, \quad N_2 = \frac{1}{A} \frac{\partial \delta K_q}{\partial P_0}. \quad (109)$$

The novel function N_2 , for example, gives us a measure of the change in energy, and hence temperature, at various points in the system in response to the applied laser heating. We discuss this connection later.

All of these can be expressed in terms of a convenient energy denominator:

$$\begin{aligned} \Delta &= \left(1 - i\omega\tau + i \frac{D_Q q^2}{\omega} \right) \left(1 - i\omega\tau + i \frac{D_c q^2}{\omega} \right) \\ &+ \xi D_c D_Q \frac{q^4}{\omega^2}, \end{aligned} \quad (110)$$

where the dimensionless coupling constant between the charge and heat modes is expressible through the high frequency figure of merit equation (69) as

$$\xi = \frac{\langle \Phi^{xx} \rangle_0^2}{\langle \Theta^{xx} \rangle_0 \langle \tau^{xx} \rangle_0} = \frac{Z^* T}{Z^* T + 1}. \quad (111)$$

We list the finite \vec{q} , ω Onsager coefficients:

$$\begin{aligned}
L_{11} &= \frac{1}{\Delta} \frac{\tau \langle \tau^{xx} \rangle_0}{\Omega} \left[1 - i\omega\tau + i(1 - \xi) D_Q \frac{q^2}{\omega} \right], \\
L_{12} &= \frac{1}{\Delta} \frac{\tau \langle \Phi^{xx} \rangle_0}{\Omega} [1 - i\omega\tau], \\
L_{22} &= \frac{1}{\Delta} \frac{\tau \langle \Theta^{xx} \rangle_0}{\Omega} \left[1 - i\omega\tau + i(1 - \xi) D_c \frac{q^2}{\omega} \right], \\
M_1 &= -\frac{1}{\Delta} D_Q \frac{q}{\omega} [1 - i\omega\tau] \frac{\langle \Phi^{xx} \rangle_0}{\langle \Theta^{xx} \rangle_0}, \\
M_2 &= -\frac{1}{\Delta} D_Q \frac{q}{\omega} \left[1 - i\omega\tau + i(1 - \xi) D_c \frac{q^2}{\omega} \right], \\
N_1 &= -\frac{q}{\omega} M_1, \\
N_2 &= \frac{i}{\omega} - \frac{q}{\omega} M_2. \tag{112}
\end{aligned}$$

The coefficient L_{ij} has the standard meanings that we have commented upon earlier. The coefficients M_1 , M_2 , N_2 , etc are the response coefficients to the applied power source. It is easy to see that these dynamical results satisfy the sum rules in equations (64)–(67).

We note several points about this exercise next.

1. The above expressions are written in terms of energy variables. It is more rigorous as well as profitable to view the transport processes as primarily those of charge and energy, rather than temperature. While we can always define an energy fluctuation, it translates to a temperature pulse only under conditions of local equilibrium, which might not always be attainable.
2. These coupled equations have a similarity to those in the description of the two coupled fluids in ^4He [61]. For insulators, the coupling between the lattice energy modes and lattice displacement modes [60, 62] also has a formally similar structure. In these cases, the role of our coupling parameter ξ is played by the dimensionless constant $C_p/C_v - 1$.
3. The new response functions M_j , N_j shed some light on pulse probe type experiments. The coefficient N_2 in equation (109) is of particular interest. In an experiment with pulsed laser heating, one would use the coefficient N_2 to compute the induced energy change δK_q . This fluctuation is interpretable as a temperature variation only if the frequency is low enough to achieve local equilibrium, but is always definable as a mechanical response function. With the help of a model of the above type, it can be used to extract the diffusion constant and hence the thermal conductivity.
4. For illustration of the above comment, if we turn off the coupling between the charge and energy modes (set $\xi = 0$) then $N_2 \rightarrow i(1 - i\omega\tau)/(\omega - i\omega^2\tau + iD_Q q^2)$. By cross multiplying we can rewrite this in the suggestive form $[\omega + i(D_Q q^2/(1 - i\omega\tau))] \delta K_q = iP_0 A$. If we take the limit of a slow response then we may express the fluctuation in terms of the temperature fluctuation $\delta K_q = C(T) \delta T_q$.

This can be seen to be of the form proposed by Cattaneo [63] as an improvement of Fourier's law²⁰.

5. In the decoupled limit $\xi = 0$, we find $L_{22} = \tau \langle \Theta^{xx} \rangle_0 / \Omega (1 - i\omega\tau + iD_Q q^2 / \omega)$. The form of L_{22} displays the possibility of a propagating mode for $\omega\tau \gg 1$, with a dispersion $\omega \sim |q| \sqrt{D_Q / \tau}$, corresponding to a second sound. The velocity of the second sound in this simplified model is also expressible in terms of the average of the Θ^{xx} operator from equation (107).
6. We see from this framework that one may devise experiments to isolate and measure different terms in the response functions. In particular, the thermal sum rule in equation (65) is given in terms of the expectation of $\langle \Theta^{xx} \rangle$, and one might ask how this can be measured. In response to a $\delta(t)$ pulse of temperature, the induced heat current pulse in the time domain jumps at $t = 0$ and the magnitude of the jump is free from τ and a function of $\langle \Theta^{xx} \rangle$ only. Similarly the energy density (hence the local reflectivity) contains an initial $t\theta(t)$ linear rise²¹.
7. In the decoupled limit, the electrical conductivity $\sigma_{xx}(\omega) = \frac{\sigma_0}{1 - i\omega\tau + iD_c q^2 / \omega}$, with $\sigma_0 = \tau \langle \tau^{xx} \rangle_0 / \Omega$. Hence the dielectric function $\epsilon(q, \omega) = 1 + \frac{4\pi i}{\omega} \sigma$ has the correct limiting forms for a metal in both static and plasmon limits. In the static limit we find the screening behaviour $\epsilon = 1 + \frac{4\pi q_e^2}{q^2} \frac{dn}{d\mu}$. For large frequencies $\omega\tau \gg 1$ we get the plasmon behaviour $\epsilon = 1 - \frac{\omega_p^2}{\omega^2}$ with $\omega_p^2 = \frac{4\pi}{\Omega} \langle \tau^{xx} \rangle_0$.
8. For a dense metallic system we are usually in the limit where the energy scales are such that $q v_F \gg \omega$, so that it is a good approximation to regard the charge redistribution as almost instantaneous compared with the heat diffusion. More formally in the decoupled limit we can see that the current response can be written in suggestive alternate forms

$$\begin{aligned}
\delta J_q &= \frac{\tau \langle \tau^{xx} \rangle_0}{1 - i\omega\tau + i \frac{D_c q^2}{\omega}} i q [\phi_q] \\
&= \frac{\tau \langle \tau^{xx} \rangle_0}{1 - i\omega\tau} i q \left[\phi_q + \frac{1}{q_e^2 \Omega} \frac{d\mu}{dn} \delta \rho_q \right]. \tag{113}
\end{aligned}$$

We have used the conservation law to go from the first form to the second. If we assume very fast relaxation of the charges, then the term in square brackets can be rewritten approximating the $\delta \rho_q$ term by its static counterpart, resulting in the familiar *electrochemical potential* $-\nabla(\phi + \frac{1}{q_e} \mu[n(r)])$. However, for poorly screened low density electron systems and for narrow band systems, it is better to avoid this approximation.

²⁰ The standard argument for the Cattaneo equation is that Fourier's law is replaced by $(1 + \tau(\partial/\partial t)) J_x^Q = \Omega \kappa(0) (-\nabla T)$, where $\kappa(0)$ is the dc thermal conductivity. Combining with the energy conservation law (equation (103)) and further writing all variations in terms of those of the temperature δT_q as $\delta K_q = C(T) \delta T_q$, we find $C(T) \left[\omega + \frac{i\kappa(0)\Omega q^2}{C(T)(1 - i\omega\tau)} \right] = iA P_0$, which is the same as the previous result on using the relation $\kappa(0) = D_Q C(T) / \Omega$.

²¹ In the decoupled limit, the energy density satisfies an equation (in space-time variables) $\frac{\partial^2}{\partial t^2} K(\vec{x}, t) = \frac{D}{\tau} \frac{\partial^2}{\partial x^2} K(\vec{x}, t) - \frac{1}{\tau} \frac{\partial}{\partial t} K(\vec{x}, t) + \frac{\langle \Theta^{xx} \rangle}{\Omega} (-\nabla^2 \psi)$. From this we see that a $\delta(t)$ pulse in a spatially varying ψ would give an initial linear rise in the energy $\sim t\theta(t)$, with a slope that is inertial, i.e. independent of τ .

9. These dynamical expressions have the property that the Seebeck coefficient and the Lorentz number are frequency independent, and hence the high frequency approximation (equation (69)) is exact here.

Thus we see that these simple equations illustrate the meaning and possible applications of energy transport in novel situations. We can make contact with standard transport theory in the limit of slow long wavelength variations, where we have argued that the Luttinger field is equivalent to a temperature field through $\nabla\psi(r) = \nabla T(r)/T$.

6. Conclusions

In this paper we have presented the basic ideas of a novel approach to computing certain interesting transport coefficients for correlated systems. These include the important Seebeck coefficient and the figure of merit. Our basic formalism extends the idea first used by Luttinger, namely, that a gravitational field can be used as a mechanical proxy for temperature gradients. We take this viewpoint further to include arbitrary time variations, thereby enabling an exploration of the regions of frequency that are normally precluded in dealing with temperature variations. This leads to the recognition of a new sum rule for thermal conductivity, as well as the application of high frequency ideas to compute the response functions mentioned above. We describe quantitative applications of these ideas in the context of the properties of the recently found sodium cobaltate materials.

A well-defined program to correct the high frequency results for the effects of finite frequency and hence to approach the transport limit is formulated and illustrated. A simple phenomenological framework with the novel response functions M_j, N_j is described, where the role of the newly defined operators becomes clear. This framework, and its many possible extensions to include other densities, should be useful in formulating the new class of experiments made possible by pulsed laser heating.

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