# Thermal transport and nonmechanical forces in metals

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We discuss contributions to the thermopower in an electron fluid. A simple argument based on Newton's second law with the pressure gradient as the force suggests that the thermopower is given by a thermodynamic derivative, viz., the entropy per particle, rather than being an independent transport coefficient. The resolution is the existence of an entropic force that results from a coupling between the mass current and the heat current in the fluid. We also discuss and clarify some aspects of a recent paper [Phys. Rev. B 102, 214306 (2020)] that provided a method for exactly solving electronic transport equations in the low-temperature limit.

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### I. INTRODUCTION

# A. Transport coefficients

Consider the number current density  $j_n$  and the heat or entropy current density  $j_s$  in a Fermi liquid without momentum conservation. These currents are driven by gradients of the chemical (or electrochemical) potential  $\mu$  and the temperature T, and the relevant transport coefficients  $L_{ij}$  are defined by the linear-response relations [1,2]

$$\dot{j}_n = \frac{-L_{11}}{T} \nabla \mu - \frac{L_{12}}{T^2} \nabla T, \tag{1.1a}$$

$$\dot{\mathbf{j}}_s = \frac{-L_{21}}{T} \nabla \mu - \frac{L_{22}}{T^2} \nabla T.$$
(1.1b)

Of the four transport coefficients, only three are independent, since an Onsager reciprocal relation requires  $L_{21} = L_{12}$ . The independent coefficients are given by Kubo formulas [2,3] that describe density-current-density-current correlations (for  $L_{11}$ ), density-current-heat-current correlations (for  $L_{12}$ ), and heat-current-heat-current correlations (for  $L_{22}$ ), respectively. In a kinetic-theory framework they take the form of different matrix elements of the inverse collision operator [4,5]. They determine the electrical conductivity  $\sigma$ , the thermopower or Seebeck coefficient  $\mathfrak{S}$ , and the heat conductivity  $\kappa$  via

$$\sigma = e^2 L_{11}/T, \tag{1.2a}$$

$$-e\mathfrak{S} = L_{12}/T L_{11}, \tag{1.2b}$$

$$\kappa = \frac{1}{T^2} [L_{22} - (L_{12})^2 / L_{11}],$$
(1.2c)

with e the electron charge. The subtraction term in Eq. (1.2c)arises if one defines the heat or thermal conductivity  $\kappa$  in the absence of a number current, as we do here following Refs. [2,6]. The quantity  $L_{22}/T^2$  by itself defines a different heat transport coefficient that was denoted by  $\sigma_h$  in Ref. [7].

## B. A simple argument for the thermopower

An elementary argument for the thermopower can be constructed as follows. The electron mass current density is  $j_m = mj_n$ , with m the electron mass. Let  $\tau$  be the momentum relaxation time, which can be due to electron-impurity scattering, or electron-phonon scattering, or any combination of scattering processes that do not conserve the electronic momentum. Then the equation of motion for  $j_m$  is, by Newton's second law,

$$\partial_t \mathbf{j}_m = \frac{-1}{\tau} \mathbf{j}_m + \frac{1}{V} \mathbf{F},\tag{1.3}$$

with V the system volume and F the total force on the electron system [8]. One contribution to the force density is the negative pressure gradient

$$\boldsymbol{F}_p/V = -\nabla p,\tag{1.4}$$

where p is the electronic contribution to the pressure. Let us assume for now that this is the only contribution to the force, as would be the case in a purely mechanical description of the fluid. In steady state,  $\partial_t \mathbf{j}_m = 0$ , Eq. (1.3) then yields

$$j_{n} = -\frac{\tau}{m} \nabla p$$

$$= -\frac{\tau}{m} \left( \frac{\partial p}{\partial \mu} \right)_{T,V} \nabla \mu - \frac{\tau}{m} \left( \frac{\partial p}{\partial T} \right)_{\mu,V} \nabla T$$

$$= -\frac{n\tau}{m} \nabla \mu - \frac{s\tau}{m} \nabla T. \tag{1.5}$$

Here, n = N/V and s = S/V are the number density and entropy density, respectively, and in going from the second line to the third one we have used the fact that the pressure derivatives at constant volume are just derivatives of the grand canonical potential  $\Omega = -pV$ . We note that the thermodynamics of a Fermi liquid with a short-ranged interaction apply since the effective force on the electrons is the unscreened external force [9]. Comparing with Eq. (1.1a) we find for the electrical conductivity the Drude formula

$$\sigma = ne^2 \tau / m, \tag{1.6}$$

and for the thermopower

$$-e\mathfrak{S} = s/n = S/N. \tag{1.7}$$

That is, according to this simple argument the thermopower is given by a thermodynamic derivative, namely, the electronic entropy per particle. This is because  $L_{11}$  and  $L_{12}$  are given by thermodynamic derivatives multiplying the same relaxation time  $\tau$ , and therefore their ratio is simply a thermodynamic derivative. This is at odds with the fact  $L_{11}$  and  $L_{12}$  are independent transport coefficients.

Since  $L_{11}$  and  $L_{12}$  both describe the response of the same current to a driving force, there is only one relaxation time that can appear in Eq. (1.5). The conclusion is therefore that there must be another contribution to the force in Eq. (1.3) that has nothing to do with the pressure gradient. In the next section we will use kinetic theory to elucidate the nature of this nonmechanical or entropic force.

## II. MASS TRANSPORT FROM KINETIC THEORY

#### A. Linearized kinetic equation

In order to derive a kinetic theory for the mass or number current density, we recall the formalism developed in Refs. [5,10]. Let

$$f_{\rm eq}(\mathbf{p}) = \frac{1}{e^{\xi_p/T} + 1}$$
 (2.1)

be the equilibrium Fermi-Dirac distribution. Here,  $\xi_p = \epsilon_p - \mu$ , with  $\mu$  the chemical potential and  $\epsilon_p$  the equilibrium single-particle energy. Here, and in what follows, "particle" means quasiparticle in the sense of Landau Fermi-liquid (LFL) theory [11,12]. For simplicity we consider spinless fermions, and we keep only the first two LFL parameters,  $F_0$  and  $F_1$ . Let f(p, x, t) be the  $\mu$ -space or single-particle phase space distribution function, consider small deviations from equilibrium,

$$f(\mathbf{p}, \mathbf{x}, t) = f_{eq}(\mathbf{p}) + \delta f(\mathbf{p}, \mathbf{x}, t), \qquad (2.2a)$$

and write  $\delta f$  as

$$\delta f(\mathbf{p}, \mathbf{x}, t) = w(\mathbf{p})\phi(\mathbf{p}, \mathbf{x}, t), \tag{2.2b}$$

with

$$w(\mathbf{p}) = -\partial f_{eq}(\mathbf{p})/\partial \epsilon_p = \frac{1}{T} f_{eq}(\mathbf{p})[1 - f_{eq}(\mathbf{p})]$$
$$= \frac{1}{4T \cosh^2(\xi_p/2T)}.$$
 (2.2c)

It is useful to define a scalar product in the space of p-dependent functions that employs w as a weight:

$$\langle g(\boldsymbol{p})|h(\boldsymbol{p})\rangle = \frac{1}{V} \sum_{\boldsymbol{p}} w(\boldsymbol{p})g(\boldsymbol{p})h(\boldsymbol{p}).$$
 (2.3)

In terms of this scalar product we can write density fluctuations as

$$\delta n(\mathbf{x}, t) = \langle 1 | \phi(\mathbf{x}, t) \rangle. \tag{2.4}$$

Similarly, we can write velocity fluctuations as

$$\delta u(x,t) = \frac{1}{nm} \langle \boldsymbol{p} | \phi(x,t) \rangle, \qquad (2.5a)$$

or, equivalently, the mass current density as

$$\mathbf{j}_{m}(\mathbf{x},t) = \langle \mathbf{p} | \phi(\mathbf{x},t) \rangle. \tag{2.5b}$$

Finally, temperature fluctuations, fluctuations of the entropy density s = S/V, and pressure fluctuations can be written as (see Ref. [10] for derivations)

$$\delta T(\mathbf{x}, t) = \frac{1}{c_V} \langle a_5(\mathbf{p}) | \phi(\mathbf{p}, \mathbf{x}, t) \rangle, \qquad (2.6a)$$

$$\delta s(\mathbf{x}, t) = \langle \epsilon_p | \phi(\mathbf{p}, \mathbf{x}, t) \rangle - \mu \, \delta n(\mathbf{x}, t), \tag{2.6b}$$

$$\delta p(\mathbf{x}, t) = \left(\frac{\partial p}{\partial T}\right)_{N,V} \delta T(\mathbf{x}, t) + \left(\frac{\partial p}{\partial n}\right)_{T,V} \delta n(\mathbf{x}, t). \quad (2.6c)$$

Here,  $c_V$  is the specific heat at constant volume, and

$$a_5(\mathbf{p}) = \epsilon_p - \langle \epsilon_p | 1 \rangle / \langle 1 | 1 \rangle.$$
 (2.7a)

The functions

$$a_1(\mathbf{p}) \equiv 1,\tag{2.7b}$$

$$a_{2,3,4}(\mathbf{p}) = p_x, p_y, p_z,$$
 (2.7c)

together with  $a_5(\mathbf{p})$  constitute the five hydrodynamic modes. They are mutually orthogonal with respect to the scalar product defined in Eq. (2.3), and their normalizations are given by [10]

$$\langle 1|1\rangle = (\partial n/\partial \mu)_{T,V}(1+F_0), \qquad (2.8a)$$

$$\langle \mathbf{p} | \mathbf{p} \rangle = 3nm^*, \tag{2.8b}$$

$$\langle a_5(\mathbf{p})|a_5(\mathbf{p})\rangle = c_V T, \qquad (2.8c)$$

with  $m^* = m(1 + F_1/3)$  the quasiparticle effective mass.

Performing a Fourier transform in space and time, with k the wave number and  $\omega$  the frequency, we can write the linearized kinetic equation for the  $\mu$ -space distribution function in the form [5,10]

$$\left[-i\omega - \Lambda(\mathbf{p}) + L_{\mathbf{k}}^{(1)}(\mathbf{p})\right] |\phi(\mathbf{p}, \mathbf{k}, \omega)\rangle = 0. \tag{2.9}$$

Here,  $\Lambda(p)$  is the collision operator, and

$$L_{k}^{(1)}(\mathbf{p}) = i\mathbf{k} \cdot \mathbf{v}_{p} + \frac{F_{0}}{\langle 1|1\rangle} |i\mathbf{k} \cdot \mathbf{v}_{p}\rangle\langle 1|$$

$$+ \frac{F_{1}}{\langle \mathbf{p}|\mathbf{p}\rangle} |(i\mathbf{k} \cdot \mathbf{v}_{p})\mathbf{p}\rangle \cdot \langle \mathbf{p}|$$
(2.10)

is a kinetic operator linear in k that comprises the streaming term and the Fermi-liquid interaction.  $v_p = p/m^*$  is the quasiparticle velocity. We are interested in a physical situation where particle number and energy are conserved,

$$\Lambda(\mathbf{p})|1\rangle = \Lambda(\mathbf{p})|a_5(\mathbf{p})\rangle = 0, \qquad (2.11a)$$

but momentum is not,

$$\Lambda(\mathbf{p})|\mathbf{p}\rangle \neq 0. \tag{2.11b}$$

## B. Kinetic equation for the mass current

We are interested in a mass current driven by gradients of the chemical potential, or the density, and the temperature. Accordingly, we want to derive an effective theory that explicitly keeps the five hydrodynamic modes. To this end, we define a projection operator

$$\mathcal{P} = \sum_{\alpha=1}^{5} |a_{\alpha}\rangle \frac{1}{\langle a_{\alpha} | a_{\alpha}\rangle} \langle a_{\alpha} | \qquad (2.12a)$$

that projects on the hydrodynamic space  $\mathcal{L}_h$  spanned by the hydrodynamic modes, and another projection operator

$$\mathcal{P}_{\perp} = \mathbb{1} - \mathcal{P} \tag{2.12b}$$

that projects onto the space  $\mathcal{L}_{\perp}$  that is orthogonal to  $\mathcal{L}_{h}$ . Operating from the left with  $\langle \boldsymbol{p}|\mathcal{P}$  on Eq. (2.9), and using  $\mathcal{P} + \mathcal{P}_{\perp} = \mathbb{1}$  yields

$$(-i\omega + 1/\tau_0) \mathbf{j}_m = -\langle \mathbf{p} | L_k^{(1)} \mathcal{P} | \phi \rangle + \langle \mathbf{p} | \Lambda \mathcal{P}_\perp | \phi \rangle$$
$$-\langle \mathbf{p} | L_k^{(1)} \mathcal{P}_\perp | \phi \rangle, \tag{2.13a}$$

where

$$\frac{1}{\tau_0} = \frac{-1}{\langle \boldsymbol{p} | \boldsymbol{p} \rangle} \langle \boldsymbol{p} | \Lambda(\boldsymbol{p}) | \boldsymbol{p} \rangle \tag{2.13b}$$

is a bare relaxation rate for the mass current. Operating on Eq. (2.9) from the left with  $\mathcal{P}_{\perp}$ , and again using  $\mathcal{P} + \mathcal{P}_{\perp} = \mathbb{1}$ , allows us to express  $\mathcal{P}_{\perp}|\phi\rangle$  in terms of  $\boldsymbol{j}_m$  and  $\mathcal{P}|\phi\rangle$ :

$$\mathcal{P}_{\perp}|\phi\rangle = G \mathcal{P}_{\perp} \Lambda |\mathbf{p}\rangle \cdot \frac{1}{\langle \mathbf{p}|\mathbf{p}\rangle} \mathbf{j}_{m} - G \mathcal{P}_{\perp} L_{k}^{(1)} \mathcal{P}|\phi\rangle. \quad (2.14)$$

Here, we have defined a propagator

$$G(\mathbf{p}, \mathbf{k}, \omega) = \left[ -i\omega - \mathcal{P}_{\perp} \Lambda(\mathbf{p}) \mathcal{P}_{\perp} + \mathcal{P}_{\perp} L_{\mathbf{k}}^{(1)}(\mathbf{p}) \mathcal{P}_{\perp} \right]^{-1}.$$
(2.15a)

For later reference we expand G to linear order in the wave number k.

$$G = G_0 - G_0 \mathcal{P}_{\perp} L_k^{(1)} \mathcal{P}_{\perp} G_0 + O(k^2), \tag{2.15b}$$

where

$$G_0(\mathbf{p}, \omega) = [-i\omega - \Lambda_{\perp}(\mathbf{p})]^{-1}$$
 (2.15c)

and  $\Lambda_{\perp} = \mathcal{P}_{\perp} \Lambda \mathcal{P}_{\perp}$ .

## C. Analysis of the equation for the mass current

Consider the right-hand side of Eq. (2.13a). To zeroth order in a gradient expansion the only contribution is from the second term with  $G_0$  substituted for G in Eq. (2.14). This term is proportional to  $j_m$ , and thus a contribution to the relaxation rate. To first order in a gradient expansion, all three terms formally contribute. However, the part of the third one that is formally of O(k) is proportional to  $j_m$ , and in steady state ( $\omega = 0$ ) the mass current itself is proportional to k. The third term therefore is effectively of  $O(k^2)$ . The equation for the mass current to linear order in the gradients thus reads

$$-i\omega \, j_m = \frac{-1}{\tau} j_m + f_1 + f_2, \tag{2.16}$$

where

$$\frac{1}{\tau} = \frac{1}{\tau_0} - \frac{1}{\langle \boldsymbol{p} | \boldsymbol{p} \rangle} \langle \boldsymbol{p} | \Lambda G_0 \mathcal{P}_{\perp} \Lambda | \boldsymbol{p} \rangle. \tag{2.17}$$

Of the two force density terms, the first one is

$$f_{1} = -\langle \mathbf{p} | L_{\mathbf{k}}^{(1)} \mathcal{P} | \phi \rangle$$

$$= -i\mathbf{k} \left[ \frac{n}{(\partial n/\partial \mu)_{TV}} \delta n + \left( \frac{\partial p}{\partial T} \right)_{NV} \delta T \right], \quad (2.18)$$

where we have used the expression (2.12a) for the projection operator and various of the thermodynamic identities derived in Appendix A of Ref. [10]. Transforming back to real space and using general thermodynamic identities as well as Eq. (2.6c), this can be written

$$f_1(x,t) = -\nabla p(x,t).$$
 (2.19)

We see that  $f_1$  is the density of the mechanical or Newtonian force  $F_p$  from Eq. (1.4).

The second force density term is

$$f_{2} = -\langle \boldsymbol{p} | \Lambda G_{0} \mathcal{P}_{\perp} L_{\boldsymbol{k}}^{(1)} \mathcal{P} | \phi \rangle$$

$$= -\langle \boldsymbol{p} | \Lambda \Lambda_{\perp}^{-1} | i(\boldsymbol{k} \cdot \boldsymbol{v}_{p}) \psi_{5}^{L(0)} \rangle \frac{1}{T} \delta T. \qquad (2.20a)$$

Here,

$$\psi_5^{L(0)}(\mathbf{p}) = a_5(\mathbf{p}) - \frac{T}{n} \left(\frac{\partial p}{\partial T}\right)_{N,V}$$
$$= \epsilon_p - (Ts/n + \mu) \tag{2.20b}$$

is the heat mode from Eq. (3.16) in Ref. [10], and the ket vector in Eq. (2.20a) is the divergence of the heat current (see Appendix B in Ref. [10]). The inverse projected collision operator  $\Lambda_{\perp}^{-1}$  acting on the heat current is to be interpreted as follows. Let  $|x\rangle = \Lambda_{\perp}^{-1} |v_p \psi_5^{L(0)}\rangle$ . Then  $|x\rangle$  is the solution of the integral equation

$$\Lambda_{\perp}|x\rangle = \left|\boldsymbol{v}_{p}\psi_{5}^{\mathrm{L}(0)}\right\rangle,\tag{2.21}$$

with the solution made unique by the requirement  $|x\rangle \in \mathcal{L}_{\perp}$ . Transforming back to real space we have

$$f_2(\mathbf{x},t) = \frac{-1}{3T} \langle \mathbf{p} | \Lambda(\mathbf{p}) \Lambda_{\perp}^{-1}(\mathbf{p}) | \mathbf{v}_p \psi_5^{L(0)}(\mathbf{p}) \rangle \nabla T(\mathbf{x},t).$$
 (2.22)

Note that  $f_2$  is a pure temperature gradient and involves no density gradient. The prefactor is a matrix element that involves a heat current and a mass current.  $f_2$  thus results from the coupling between the number density and the heat mode and represents a nonmechanical or entropic force. It is generically nonzero, but vanishes for simple model collision operators where  $\Lambda\Lambda_{-}^{-1}|\mathbf{v}_p\psi_5^{\mathrm{L}(0)}\rangle\propto|\mathbf{v}_p\psi_5^{\mathrm{L}(0)}\rangle$ , since the mass and heat currents are mutually orthogonal.

# D. Contributions to the thermopower

By comparing the coefficients in Eqs. (1.1a) and (2.16), with  $f_1$  and  $f_2$  from Eqs. (2.19) and (2.22), respectively, we can determine the Onsager coefficients  $L_{11}$  and  $L_{12}$  that determine the electrical conductivity  $\sigma$  and the thermopower  $\mathfrak{S}$  according to Eqs. (1.2). For the former we obtain the Drude

formula (1.6), with  $\tau$  given by Eq. (2.17). For the latter we find

$$-e\mathfrak{S} = \frac{S}{N} + \frac{1}{3nT\tau} \langle \boldsymbol{p} | \Lambda \Lambda_{\perp}^{-1} | \boldsymbol{v}_p \psi_5^{L(0)} \rangle, \tag{2.23}$$

which is Eq. (1.7) augmented by a contribution from the entropic force.

#### III. EXAMPLES

An evaluation of the entropic force for a given collision operator involves solving the integral equation (2.21). This is equivalent to solving the Boltzmann equation with the same collision operator. Alternatively, one can employ the hydrodynamic theories developed in Refs. [5,10]. In this section we use two common scattering processes to illustrate how the entropic force contributes to the thermopower.

# A. Disordered Fermi liquid

As a simple example, consider the case of a Fermi liquid in the presence of quenched disorder. In this case, particle number and energy are conserved, but momentum is not, as we have assumed in Eqs. (2.11). Hydrodynamic equations for this problem were derived in Ref. [5]. Within this hydrodynamic formalism, the result for the Onsager coefficients  $L_{11}$  and  $L_{12}$  is [see Eqs. (3.22) and (3.23) in Ref. [5]]

$$L_{11} = \frac{-T}{m^2} \langle \hat{\boldsymbol{k}} \cdot \boldsymbol{p} | \Lambda^{-1}(\boldsymbol{p}) | \hat{\boldsymbol{k}} \cdot \boldsymbol{p} \rangle, \tag{3.1a}$$

$$L_{12} = \frac{-T}{m^2} \langle \hat{\boldsymbol{k}} \cdot \boldsymbol{p} | \Lambda^{-1}(\boldsymbol{p}) | (\hat{\boldsymbol{k}} \cdot \boldsymbol{p}) (\epsilon_p - \mu) \rangle. \quad (3.1b)$$

Here, the collision operator describes both electron-impurity scattering and electron-electron scattering, and its inverse exists in this context since none of the vectors in the matrix elements are conserved quantities. The two coefficients are given by different matrix elements of the inverse collision operator, and thus in general are independent. However, for the simplest possible model of a constant relaxation rate,

$$\Lambda = \frac{-1}{\tau} \left[ \mathbb{1} - \frac{|1\rangle\langle 1|}{\langle 1|1\rangle} - \frac{|a_5\rangle\langle a_5|}{\langle a_5|a_5\rangle} \right],\tag{3.2}$$

the rate drops out of the ratio  $L_{12}/L_{11}$  and performing the integrals yields

$$-e\mathfrak{S} = \frac{\pi^2}{2}T/\epsilon_{\rm F},\tag{3.3}$$

which is equal to the entropy per particle of a Fermi liquid in the low-temperature limit [12,13]. For this simple model collision operator we thus recover the result (1.7) of the naive argument in Sec. IB. This is consistent with the analysis in Sec. II C: With Eq. (3.2) for the collision operator, the solution of Eq. (2.21) is  $|x\rangle = -\tau |v_p \psi_5^L(0)\rangle$ , and hence the entropic force, Eq. (2.22), vanishes.

This is no longer true, even within a simple relaxation-time model, if we allow for an energy dependence of the relaxation time. For instance, if we replace  $1/\tau$  in Eq. (3.2) by [14]

$$\frac{1}{\tau(\epsilon_p)} = \frac{1}{\tau} \sqrt{\epsilon_p/\epsilon_F} \tag{3.4}$$

and evaluate the integrals in Eqs. (3.1), we obtain Wilson's result [14]

$$-e\mathfrak{S} = \frac{\pi^2}{3}T/\epsilon_{\rm F},\tag{3.5}$$

consistent with the fact that now the entropic force is no longer zero.

### **B.** Electron-phonon scattering

As another example we consider the electron-phonon scattering problem with the commonly used assumption that the phonons remain in equilibrium [2,14]. In Ref. [7] we provided an exact solution of integral equations for transport coefficients based on the Boltzmann equation. However, the equations solved were not quite equivalent to the Boltzmann equation since in their derivation various factors of the electron momentum p were replaced by the Fermi momentum  $p_F$ . As a result of this approximation the Onsager relation  $L_{21} = L_{12}$  was violated, and the results for the transport coefficients were different from what is obtained from the Boltzmann equation proper. However, the solutions of the integral equations as written were exact. Here, we discuss the changes that result from not making this approximation.

Within the formalism of Ref. [7] the Onsager coefficients  $L_{11}$  and  $L_{12}$  are are given by

$$L_{11} = \frac{nT}{m} \langle v^3 | \varphi_0 \rangle, \tag{3.6a}$$

$$L_{12} = \frac{nT}{m} \langle v^3 | \varphi_1 \rangle, \tag{3.6b}$$

where

$$\nu(\epsilon) = \sqrt{1 + \epsilon/\epsilon_{\rm F}},\tag{3.7}$$

and the functions  $\varphi_0$  and  $\varphi_1$  are the solutions of integral equations

$$\Lambda(\epsilon)\varphi_0(\epsilon) = -\nu(\epsilon), \tag{3.8a}$$

$$\Lambda(\epsilon)\varphi_1(\epsilon) = -\epsilon \,\nu(\epsilon),\tag{3.8b}$$

with  $\Lambda$  a collision operator. The factors  $\nu(\epsilon)$  on the right-hand sides of Eqs. (3.8) result from a factor  $p_F/p$  that appears in the angular integrations that reduce the linearized Boltzmann equation to a one-dimensional integral equation [see Eqs. (C2a) and (C3) in Ref. [7]] [15]. The  $\nu^3$  in Eqs. (3.6) result from one factor of  $p/p_F$  in the radial p-integration measure, and one factor of  $p/p_F$  from each of the two current vertices. All of these factors were approximated by  $\nu(\epsilon) \approx 1$  in Ref. [7].

The Onsager coefficients  $L_{21}$  and  $L_{22}$  can also be obtained from the solutions of Eqs. (3.8):

$$L_{21} = \frac{nT}{m} \langle \epsilon \, v^3 | \varphi_0 \rangle, \tag{3.9a}$$

$$L_{22} = \frac{nT^2}{m} \langle \epsilon \, v^3 | \varphi_1 \rangle. \tag{3.9b}$$

The collision operator  $\Lambda$  is given by

$$\Lambda(\epsilon) = \int du [K(\epsilon, u) R_{\epsilon \to u} - K_0(\epsilon, u)], \qquad (3.10)$$

with  $R_{\epsilon \to u} f(\epsilon) = f(u)$  the replacement operator. The kernel K has three contributions,

$$K(\epsilon, u) = K_0(\epsilon, u) - K_1(\epsilon, u) - K_2(\epsilon, u). \tag{3.11}$$

 $K_0$  and  $K_1$  are given by Eqs. (2.18a)–(2.18c) in Ref. [7].  $K_2$  gets modified by a factor of  $(p_{\rm F}/p)^2$  in the last line of Eq. (C3) in that reference that also had been approximated by 1. This leads to

$$K_2(\epsilon, u) = \frac{1}{2} \left( 1 - \frac{T_1^2}{2\epsilon_F^2} \right) \left( \frac{u - \epsilon}{T_1} \right)^2 K_0(\epsilon, u),$$
 (3.12)

which replaces Eq. (2.18d) in Ref. [7]. Here,  $T_1$  is the bosonic energy scale that appears in the electron-phonon collision integral and is on the order of the Debye temperature [7].

The integral equations (3.8) can be solved exactly in the low-temperature limit by the same method as in Ref. [7]. The result is

$$\sigma(T \to 0) = \frac{ne^2}{m} \frac{1}{120 \,\zeta(5)g_0} \frac{1}{1 - T_1^2 / 4\epsilon_F^2} \frac{T_1^4}{T^5} + O(1/T^3),$$

(3.13a)

$$-e\mathfrak{S}(T\to 0) = \frac{\pi^2}{3} \frac{T}{\epsilon_{\rm F}} + O(T^3), \tag{3.13b}$$

$$\kappa(T \to 0)/T = \frac{n}{m} \frac{\eta}{g_0} \frac{T_1^2}{T^3} + O(1/T).$$
 (3.13c)

Here,  $g_0$  is the electron-phonon coupling constant from Eq. (2.6) in Ref. [7], and  $\eta$  is the number from Eq. (3.39b) in that paper. These results replace Eqs. (3.36a), (3.37), and (3.39a), respectively, in the same reference [16]. The Onsager relation  $L_{21} = L_{12}$  is now satisfied, and the result for the

thermopower agrees with Wilson's solution of the Boltzmann equation [14]. We emphasize that these results are exact solutions of the Boltzmann equation in the low-temperature limit. The result for the thermopower, Eq. (3.13b), is consistent with the fact that the collision operator has a complicated energy dependence and hence the entropic force, Eq. (2.22), does not vanish.

#### IV. SUMMARY AND CONCLUSION

In summary, we have identified two physically different contributions to the thermopower in a metal. One is due to the mechanical force on the electrons, i.e., the gradient of the pressure of the Fermi liquid. The other one is an entropic force that arises from the mass current coupling to the heat current. This is analogous at some level to the contributions to the sound velocity in either a classical fluid [17] or a fermionic quantum fluid [10]. A purely mechanical theory would conclude that the speed of sound is given by the isothermal compressibility of the fluid; it is the coupling to the heat mode that changes this to the adiabatic compressibility. However, an important difference is that the thermopower is a transport coefficient, whereas the speed of sound is a thermodynamic derivative; the only question is which derivative.

We also have clarified some aspects of Ref. [7], which gave a method exactly solving electronic transport problems in the low-temperature limit. Specifically, the integral equations solved exactly in that reference were not quite equivalent to the Boltzmann equation due to some approximations in the procedure that transforms the Boltzmann equation into a one-dimensional integral equation. These approximations are not necessary, and eliminating them leads to the exact solution of the Boltzmann equation proper that is given in Sec. III B.

[16] Equation (3.39a) in Ref. [7] gave a result for  $\sigma_h := L_{22}/T^2$  rather than for  $\kappa$ . The result for that quantity is

$$\sigma_h(T \to 0)/T = \frac{n}{m} \frac{1}{g_0} \left( \eta + \frac{\pi^4/9}{120\zeta(5)} \frac{T_1^2/\epsilon_{\rm F}^2}{1 - T_1^2/4\epsilon_{\rm F}^2} \right) \frac{T_1^2}{T^3} + O(1/T).$$

[17] D. Forster, Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions (Benjamin, Reading, MA, 1975).

<sup>[1]</sup> H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley, New York, 1985).

<sup>[2]</sup> G. D. Mahan, *Many-Particle Physics* (Plenum, New York, 1981).

<sup>[3]</sup> R. Kubo, J. Phys. Soc. Jpn. 12, 570 (1957).

<sup>[4]</sup> J. R. Dorfman, H. van Beijeren, and T. R. Kirkpatrick, *Contemporary Kinetic Theory of Matter* (Cambridge University Press, Cambridge, UK, 2021).

<sup>[5]</sup> T. R. Kirkpatrick and D. Belitz, Phys. Rev. B 105, 245147 (2022).

<sup>[6]</sup> J. M. Ziman, *Electrons and Phonons* (Clarendon, Oxford, UK, 1960).

<sup>[7]</sup> J. Amarel, D. Belitz, and T. R. Kirkpatrick, Phys. Rev. B 102, 214306 (2020).

<sup>[8]</sup> For the scattering processes we will consider explicitly this is the only contribution to the current. For electrons in the presence of quenched disorder this is obviously true. For electron-phonon scattering in the common approximation that treats the phonons as remaining in equilibrium it also is true. More generally, the phonons will contribute to the momentum current, and the hydrodynamic description of the coupled electron-phonon problem will be more complicated.

<sup>[9]</sup> D. Pines and P. Nozières, The Theory of Quantum Liquids (Addison-Wesley, Redwood City, CA, 1989), Chap. 3.3.

<sup>[10]</sup> D. Belitz and T. R. Kirkpatrick, Phys. Rev. B 105, 245146 (2022).

<sup>[11]</sup> E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics, Part* 2, 2nd ed. (Pergamon, Oxford, UK, 1981).

<sup>[12]</sup> G. Baym and C. Pethick, *Landau Fermi-Liquid Theory* (Wiley, New York, 1991).

<sup>[13]</sup> Here, we consider only the Fermi-liquid contribution to the entropy and neglect contributions from, e.g., impurities or phonons.

<sup>[14]</sup> A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, UK, 1954).

<sup>[15]</sup> In Ref. [7] the electron momentum was denoted by k rather than p.