Prediction of thermomagnetic and thermoelectric properties for novel materials and systems

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Abstract – We express the link between conductivity and coefficients of Seebeck, Thomson, Nernst-Ettingshausen and Reghi-Leduc via the temperature derivative of the chemical potential of a system. These general expressions are applied to three-, two- and one-dimensional systems of charge carriers having a parabolic or Dirac spectrum. The method allows for predicting thermoelectric and thermomagnetic properties of novel materials and systems.

The theory of thermoelectric (TE) and thermomagnetic (TM) phenomena in metals has been built in the 1930s–1950s [1,2]. Essentially, it is based on the kinetic approach, where more or less complicated transport equations are formulated and solved for different systems in order to obtain the transport coefficients characterizing the TE and TM effects. In the recent decades, the invention of a wide range of new materials with exotic spectra where different types of interactions can interplay (graphene and carbon nano-tubes being two examples) gave a boost to the studies of the most important TE and TM constants, such as Seebeck, Thomson, Nernst-Ettingshausen and Reghi-Leduc coefficients, thermal conductivity and Peltier tensors. Yet, the notion of a heat flow, required to find these coefficients, becomes hardly definable in the case of systems of interacting particles, which is why one can hardly rely on kinetic approaches, in general. Such a problem does not appear if one deals with the conductivity tensor which can be always calculated using either transport equations or diagrammatic approaches. Some relations between the TE and TM constants and conductivity tensor are well known for non-interacting systems with simple spectra (Wiedemann-Franz law and Mott formula), but these relations have not been generalised to the case of interacting systems with exotic spectra so far.

This work is aimed at formulating a unified approach to the description of TE and TM phenomena virtually in any electronic system based on establishing the universal links between main TE and TM coefficients and the conductivity tensor. We show that it is sufficient to know the temperature dependence of a chemical potential of a system to obtain Seebeck, Thomson and Peltier coefficients. The Nernst-Ettingshausen, Reghi-Leduc and thermal conductivity coefficients can be expressed through the conductivity tensor and thermal derivatives of the chemical potential and magnetization of the system. These relations allow for obtaining the thermoelectric and thermomagnetic properties of novel 1D and 2D systems of normal charge carriers and Dirac fermions, electron systems with topologically nontrivial spectra, etc.

We shall operate with the chemical and electro-chemical potentials of charge carriers in a wide range of systems and materials. What a wonder, these quantities have a non-unique definition in literature! Electro-chemists and soft-matter physicists usually assume that an electro-chemical potential of a system is a constant in a stationary conditions, while a chemical potential is a local characteristic which may change from point to point of a system (see, for example, [3]). In the solid-state physics, frequently, the opposite rule is postulated: a chemical potential is a characteristic of the whole system, and it is a constant in the stationary case, while the electro-chemical potential may vary from point to point (see, for example, [4]).
Table 1: The temperature dependences of chemical potentials in the systems of different dimensionalities, for carriers having a parabolic and linear dispersion, in the limits of Boltzmann and degenerate Fermi gases. $P$ and $D$ denote the expressions obtained for parabolic and Dirac dispersion cases, respectively.

| Dimensionality | $d = 3$ | $d = 2$ | $d = 1$ |
|----------------|---------|---------|---------|
| Fermi energy $\mu_p^{(d)}(0)$ (parabolic spectrum) | $\mu_p^{(3)}(0) = \frac{3\pi^2}{2m} \frac{k^2}{n_e}$ | $\mu_p^{(2)}(0) = \frac{\pi\hbar^2}{m} n_e$ | $\mu_p^{(1)}(0) = 2\pi^2 k^2 \frac{1}{m} n_e$ |
| Chemical potential for degenerated FG (parabolic spectrum) | $\mu_p^{(3)}(T) = \mu_p^{(3)}(0) - \frac{\pi^2 T^2}{6\mu_p^{(3)}(0)}$ | $\mu_p^{(2)}(T) = \mu_p^{(2)}(0) + T \ln \left[ 1 - e^{-\frac{\pi^2}{12\mu_p^{(2)}(0)}} \right]$ | $\mu_p^{(1)}(T) = \mu_p^{(1)}(0) - \frac{\pi^2 T^2}{12\mu_p^{(1)}(0)}$ |
| Chemical potential for Boltzman FG (parabolic spectrum) | $\mu_p^{(3)}(T) = -\frac{3}{2} T \ln \left( \frac{T}{\mu_p^{(3)}(0)} \right)$ | $\mu_p^{(2)}(T) = \mu_p^{(2)}(0) + T \ln \left[ 1 - e^{-\frac{\pi^2}{12\mu_p^{(2)}(0)}} \right]$ | $\mu_p^{(1)}(T) = -\frac{T}{2} \ln \frac{\pi^2}{4\mu_p^{(1)}(0)}$ |
| Fermi energy $\mu_D^{(d)}(0)$ (Dirac spectrum) | $\mu_D^{(3)}(0) = \pi \hbar c \sqrt{3n_e}$ | $\mu_D^{(2)}(0) = \frac{\pi}{2} \hbar c \sqrt{2n_e}$ | $\mu_D^{(1)}(0) = \pi \hbar c n_e$ |
| Chemical potential for degenerated FG (Dirac spectrum) | $\mu_D^{(3)}(T) = \mu_D^{(3)}(0) - \frac{\pi^2 T^2}{3\mu_D^{(3)}(0)}$ | $\mu_D^{(2)}(T) = \mu_D^{(2)}(0) - \frac{\pi^2 T^2}{12\mu_D^{(2)}(0)}$ | $\mu_D^{(1)}(T) = T \ln \left( \frac{e^{\frac{\pi^2}{12\mu_D^{(1)}(0)}} - 1}{\pi^2} \right)$ |
| Chemical potential for Boltzman FG (Dirac spectrum) | $\mu_D^{(3)}(T) = -3T \ln \left( \frac{T}{\mu_D^{(3)}(0)} \right)$ | $\mu_D^{(2)}(T) = -2T \ln \left( \frac{T}{\mu_D^{(2)}(0)} \right)$ | $\mu_D^{(1)}(T) = -T \ln \left( \frac{1}{\mu_D^{(1)}(0)} \right)$ |

Here we shall adopt the former approach, following the textbooks of Madelung [5] and Abrikosov [6], who applied the concept of local chemical potential to solid-state systems. In this approach, the system subjected to a temperature gradient is assumed to be in thermal equilibrium locally, so that in each small volume of the sample one can introduce the thermodynamic potential $\Omega[T(\mathbf{r})]$, $\mathbf{r}$ being a coordinate, the number of particles $N[T(\mathbf{r})]$ and the chemical potential

$$
\mu[T(\mathbf{r})] = -\frac{\partial \Omega}{\partial N},
$$

Defined in this way, the chemical potential may vary in real space, if the temperature of the system varies.

The electrochemical potential is defined as

$$
\varphi = \mu + e\varphi_e,
$$

with $\varphi$ being the electrostatic potential. This quantity remains constant for a whole system at stationary conditions. Physically it means that if no electric current flows through the system, its electro-chemical potential is constant, while its chemical potential can vary.

The temperature dependences of chemical potentials for normal carriers (having a parabolic dispersion) and Dirac fermions (having a linear dispersion) for the systems of different dimensionalities in the Boltzmann limit and in the limit of a degenerate Fermi gas are summarized in table 1.

We show below that this information is sufficient for the prediction of the TE and TM coefficients in a very wide variety of systems. Let us consider a conductor looped via a voltmeter in the $y$-direction, placed in the magnetic field $\mathbf{H}$ oriented along the $z$-axis, and subjected to the temperature gradient $\nabla_x T$ applied along the $x$-axis (see fig. 1). In a full generality, one can express the electric current density $\mathbf{j}$ components as

$$
\begin{pmatrix}
J_x \\
J_y
\end{pmatrix} = \sigma
\begin{pmatrix}
E_x \\
E_y
\end{pmatrix} + \beta \begin{pmatrix}
\nabla_x T \\
0
\end{pmatrix},
$$

where $\sigma$ and $\beta$ are the conductivity and the thermoelectric tensors, respectively. Further, we restrict our consideration to the limit of magnetic fields weak by a parameter $\omega_c \tau \ll 1$, where $\omega_c$ is the cyclotron frequency, and $\tau$ is the elastic scattering time. Note that the cyclotron frequency is defined differently for normal carriers (NC) having a parabolic dispersion and for Dirac fermions (DF) having a linear dispersion. Namely, for NC $\omega_c = \frac{eH}{mc}$, where $H$ is the magnetic field, $m$ is the mass of the carrier in the plane normal to the magnetic field direction, while for DF $\omega_c = \frac{eHv_F}{m}$, where $v_F$ is the Fermi velocity.

For the heat flow $q$ components one can write a similar equation:

$$
\begin{pmatrix}
q_x \\
q_y
\end{pmatrix} = \gamma
\begin{pmatrix}
E_x \\
E_y
\end{pmatrix} + \zeta \begin{pmatrix}
\nabla_x T \\
0
\end{pmatrix},
$$

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where the tensor $\gamma$ is related to $\hat{\beta}$ by means of the Onsager relation: $\gamma(H) = -T\hat{\beta}(\pm H)$. Tensor $\hat{\beta}$ is related to the tensors $\hat{\gamma}$ and $\hat{\sigma}$ mainly determines the value of thermal conductivity $\hat{\kappa}$ [6]. In the following we shall find the tensor $\hat{\beta}$ and express the most important coefficients of the TM and TE transport through its components and conductivity tensor $\hat{\sigma}$.

We limit ourselves to the consideration of the case where the electric circuits are broken in both the $x$ and $y$ directions, so that $j_x = 0$ (see fig. 1):

$$j_x = \sigma_{xx} E_x + \sigma_{xy} E_y + \beta_{xx} \nabla_x T = 0,$$

$$j_y = \sigma_{yx} E_x + \sigma_{yy} E_y + \beta_{yx} \nabla_y T = 0.$$  \hspace{1cm} (5)

The off-diagonal components of the TE tensor differ from zero only due to the non-zero magnetic field applied. They can be determined from the fourth Maxwell equation [7,8] and expressed in terms of the temperature derivative of the magnetization $M_z$:

$$\beta_{xy} = -\beta_{yx} = \frac{e}{\gamma} \frac{\partial M_z}{\partial T},$$

where the latter can be expressed as the derivative of the thermodynamic potential $\Omega$ over the magnetic field:

$$M_z = -\frac{\partial \Omega}{\partial H_z}.$$  \hspace{1cm} (6)

The electric field along the $x$-direction induced by the temperature gradient can be determined using the condition of constancy of the electrochemical potential, eq. (2):

$$\nabla \left[ e \varphi + \mu(T(x), n(x)) \right] = 0$$

and can be expressed in terms of the full derivative of the chemical potential:

$$E_x = -\nabla \varphi = \frac{1}{e} \left( \frac{\partial \mu}{\partial T} \right) \nabla_x T.$$  \hspace{1cm} (7)

Here we have assumed that the electro-neutrality of our system is preserved (except for its surfaces, maybe), and no volume charge is formed, so that $\nabla_z n = 0$. Substituting eq. (8) into the first of the set of eqs. (3) one finds that

$$\hat{\beta} = \left[ \begin{array}{ccc} \sigma_{xx} & \frac{dn}{dT} & c \frac{dM_z}{dT} \\ c \frac{dM_z}{dT} & -c \frac{dn}{dT} & \sigma_{yy} \\ -c \frac{dn}{dT} & -\sigma_{yy} & \sigma_{xx} \end{array} \right].$$  \hspace{1cm} (9)

Now we can proceed with obtaining TE and TM coefficients explicitly.

The Seebeck tensor (differential thermoelectric power) $\hat{Q}$ is related to the tensors $\hat{\beta}$ and $\hat{\sigma}$:

$$\hat{Q}(H) = -\hat{\sigma}^{-1}(H) \hat{\beta}(H) = \frac{1}{e} \left( \frac{\partial \mu}{\partial T} \right) \hat{I} - e\hat{\sigma}^{-1}c \left( \frac{dM_z}{dT} \right).$$  \hspace{1cm} (10)

where $\hat{\sigma} = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$ is the Levi-Civita tensor, $\hat{I}$ is the identity tensor.

The chemical potential derivative can be found explicitly as

$$\frac{\partial \mu}{\partial T} = 2 \frac{\partial \mu}{\partial T}. $$  \hspace{1cm} (11)

For the reference case of an isotropic 3D metal with the parabolic spectrum in zero magnetic field

$$\frac{\partial \mu}{\partial n} = \frac{\hbar^2}{m} \pi^{1/3}$$

and $dn/dT = \nu \partial \mu / \partial T$ with $\nu = n p_{F} / (\pi^2 \hbar^3)$ as the density of states. Using these expressions one finds

$$\frac{\partial \mu}{\partial T} = 2 \frac{\partial \mu}{\partial T}. $$  \hspace{1cm} (12)

The temperature derivative of a chemical potential for a degenerate electron gas is well known (see, for example, [6]):

$$\mu(T) = \mu(0) - \frac{\pi^2 T^2}{6} \nu^\prime(\mu).$$  \hspace{1cm} (13)

As in the 3D case $\nu^\prime(\mu) \sim \sqrt{\mu}$, thus $\partial \mu / \partial T = -\pi^2 T / (6 \mu)$, and consequently $dn / dT = -\pi^2 T / (3 \mu)$. This is why we obtain

$$Q(T, 0) = \frac{1}{e} \left( \frac{d\mu}{dT} \right) = \frac{\pi^2 T}{3 \epsilon^\mu}. $$

This expression exactly coincides with the Mott formula for a differential thermoelectric power [6], which demonstrates the equivalence of our approach to the classic result obtained the kinetic approach for a 3D metal.

The Thomson coefficient, which describes alternatively heating or cooling of a current carrying conductor, can be also easily expressed now in terms of $\mu$ and $M$ temperature derivatives following the Thomson relation,

$$\tilde{T} = T \frac{d\hat{Q}}{dT} + \frac{T}{e} \left( \frac{d^2 \mu}{dT^2} \right) \hat{I} - e T \hat{\sigma}^{-1} c \left( \frac{d^2 M}{dT^2} \right).$$  \hspace{1cm} (14)

In the absence of magnetic field

$$\tilde{T}(T, H = 0) = \frac{T}{e} \left( \frac{d^2 \mu}{dT^2} \right) \hat{I}. $$  \hspace{1cm} (15)
Using the expressions for the chemical potential summarized in the table one can see that the Thomson coefficient behaves quite differently for Dirac and normal carriers. For example, in the degenerate 2D gas of carriers with a parabolic dispersion the Thomson coefficient is

\[ T^{(2)}_{\nu} = \frac{\left[ \mu^{(2)}_{\nu} (0) \right]^2}{eT^2} \exp \left( -\frac{\mu^{(2)}_{\nu} (0)}{T} \right), \]  

(16)

while for 2D Dirac carriers it differs not only by its temperature dependence but also in its sign:

\[ T^{(2)}_{\nu} = -\frac{\pi^2T}{6e\mu^{(2)}_{\nu} (0)}. \]  

(17)

One can see that in a wide range of temperatures up to \( T \lesssim 0.2\mu^{(2)}_{\nu} (0) \) the Thomson coefficient for the normal carriers is exponentially small. At the same time for Dirac fermions the Thomson coefficient is of the opposite sign and grows in its absolute value linearly with temperature. Moreover, at high temperatures the behavior of the Thomson coefficient is non-monotonous for normal carriers, while for the Dirac spectrum it is a monotonous saturating function (see fig. 2).

The Nernst-Ettingshausen effect is the thermal analog of the Hall effect and it consists in the appearance of an electric field \( E_y \) perpendicular to the mutually perpendicular magnetic field \( H \) and temperature gradient (\( \nabla_z T \)) (see fig. 1). It is characterized by the Nernst coefficient

\[ \nu = \frac{E_y}{(\nabla_z T)H}, \]  

(18)

which can be expressed in terms of the resistivity and thermoelectric tensors [9]:

\[ \nu = -(\rho_{xx}\beta_{xy} + \rho_{xy}\beta_{yy})/H. \]  

(19)

Substituting in eq. (19) the expressions for the thermoelectric tensor components obtained above, we arrive at

\[ \nu = \frac{\sigma_{xx}}{e^2nc} \left( \frac{d\mu}{dT} \right) + c\rho_{yy}/H \left( \frac{dM_z}{dT} \right). \]  

(20)

The first term here is governed by the temperature dependence of the chemical potential, while the second is related to magnetization currents. In our reference case of a 3D metal the second term is negligible by a parameter \((k_F)^{-1} \ll 1\), with \( k_F \) being the Fermi wave vector, \( l \) being the mean free path. Using eq. (13) one easily reproduces the well-known Sondheimer formula [2],

\[ \nu = \frac{\sigma_{xx}}{e^2nc} \left( \frac{d\mu}{dT} \right) = -\frac{\sigma_{xx}}{e^2nc} \frac{\pi^2T}{3\mu} = -\frac{\pi^2T}{3\mu} \frac{\tau}{mc}. \]  

(21)

In fluctuating superconductors the role of the second term in eq. (20) becomes crucial: it “saves” the third law of thermodynamics in the vicinity of the second critical field

\[ H_{c2}(0) \]  

[10]. The oscillations of the Nernst-Ettingshausen coefficient in graphene obtained within the present approach [8] demonstrate a remarkable agreement with experimental data [11].

In the rest of this letter we summarize the useful expressions for other important TE and TM coefficients following the approach formulated here.

The Peltier tensor which describes the heat generation by electric current, is given by the Kelvin relation (see, e.g., [6]) and can also be expressed in terms of conductivity and thermoelectric tensors,

\[ \hat{\Pi}(T, H) = T \hat{Q}(T, H) = -T\hat{\sigma}^{-1}(H)\hat{\beta}(H). \]  

(22)

At zero magnetic field, it has only diagonal components:

\[ \Pi(T, 0) = \frac{T}{e} \left( \frac{d\mu}{dT} \right). \]  

(23)

Interestingly, while the whole system is out of thermal equilibrium in the presence of electric current, the Peltier coefficient can still be linked to the thermal derivative of the chemical potential!

The thermal conductivity tensor \( \hat{\kappa} \) describes the ability of a material subject to a temperature gradient to conduct heat. It can be expressed through the elements of the TE tensor and electric conductivity,

\[ \hat{\kappa} = -\frac{\pi^2T}{3e^2} \hat{\sigma} \left( \hat{I} - \frac{3e^2}{\pi^2} \left[ \hat{\beta}^{-1} \right]^2 \right). \]  

(24)

The Righi-Leduc effect describes the heat flow resulting from a perpendicular temperature gradient in the absence of electric current. The Righi-Leduc coefficient can be
expressed through the diagonal elements of thermal conductivity and conductivity tensors as

\[ L = \frac{\sigma_{xx}}{c_{\text{TE}}} \kappa_{yy}. \] (25)

Finally, we would like to discuss the limitations of our approach. We have largely used the electro-neutrality condition \( \nabla_x n = 0 \), which may fail in certain semiconductor systems where the volume charge effects are important. For the same reason, this approach fails to account for electric currents induced by a phonon drag.

In conclusion, the crucial function which governs all the TE and TM constants listed above is the temperature derivative of the chemical potential \( \frac{d\mu}{dT} \). This simple observation opens the way to the prediction of the TE and TM effects in new structures and materials. In particular, it shows that the TE and TM properties may be strongly different in systems with Dirac fermions and normal carriers.

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