Failure of the Wiedemann-Franz law in mesoscopic conductors

Maxim G. Vavilov and A. Douglas Stone
Department of Applied Physics, Yale University, New Haven, Connecticut 06520, USA
(Received 14 September 2005; published 7 November 2005)

We study the effect of mesoscopic fluctuations on the validity of the Wiedemann-Franz (WF) law for quasi-one-dimensional metal wires and open quantum dots. At temperatures much less than the generalized Thouless energy, $E_\tau$, the WF law is satisfied for each specific sample, but as the temperature is raised through $E_\tau$, a sample-specific correction to the WF law of order $1/g$ appears ($g$ is the dimensionless conductance) and then tends to zero again at $k_B T \approx E_\tau$. The mesoscopic violation of the Wiedemann-Franz law is even more pronounced in a ring geometry for which the Lorenz number exhibits $h/e$ flux-periodic Aharonov-Bohm oscillations.

I. INTRODUCTION

The Wiedemann-Franz (WF) law\(^1\) in macroscopic conductors relates the electrical and thermal conductivities $\sigma, \kappa$ via the condition $\kappa/\sigma T = l_0$, where the Lorenz number $l_0 = (\pi^2/3)(k_B/e)^2$ (here $k_B, e$ are Boltzmann’s constant and the electron charge). The law is satisfied with an accuracy of 5–10\% in most metals at room temperature,\(^2\) but fails in the temperature range $T = 10\text{--}100$ K where the Bloch-Gruneisen form of the resistivity holds.\(^3\) In this range, the failure is understood because inelastic phonon scattering degrades thermal and electrical currents differently. At temperatures below 10 K, when the inelastic contribution to the scattering is negligible, the law is satisfied extremely accurately\(^4\) as it follows simply from the Sommerfeld expansion of the energy-dependent conductivity, which is accurate to order $(k_B T/E_F)^2$, where $E_F$ is the Fermi energy. Failure of the WF law at low temperatures is often associated with non-Fermi-liquid behavior in strongly correlated systems.\(^5\)

In the current work we focus on the violation of the WF law induced by mesoscopic fluctuations in Fermi-liquid systems. Mesoscopic conductors are normal conductors on a micron or nanometer scale connecting bulk leads which act as thermal equilibrium reservoirs held at different voltages and temperatures. By assumption there are no inelastic scattering processes in the conductor itself, exactly the condition under which the WF law holds for macroscopic conductors. However, as is well known, each specific mesoscopic sample exhibits a fluctuating energy dependence of its conductance, which varies by $\delta G \sim e^2/h$ on an energy scale $E_c \ll E_F$.\(^6,7\) Therefore, the Sommerfeld expansion fails even when $k_B T \ll E_F$. The most immediate effect of this failure is that the thermopower coefficient, which gives the voltage induced by a temperature gradient when no electrical current flows, becomes random in sign and is enhanced by $(E_F/E_c)^{1/2}$, where $g = G/G_0$ is the dimensionless conductance and $G_0 = e^2/h$. This enhancement can be many orders of magnitude, has been discussed in a number of previous works,\(^8\)-12 and has been measured in at least one experiment on quantum dots.\(^13\)

It is straightforward to show that the violation of the WF law is not due to the enhanced thermopower coefficient and occurs at size scales for which the thermopower effect would be negligible. As usual, the mesoscopic correction to the WF law is random and arises from interference of multiple scattered electron trajectories; in a ring geometry this correction will oscillate periodically in magnetic flux with period $h/e$, making it easier to detect. Very recently thermoelectric measurements have been made in such systems,\(^14\) so experiments of this type are feasible.

We consider a two-probe measurement for which the electrical current, $I_e$, and thermal current, $I_h$, between the reservoirs at temperatures $T$ and $T + \delta T$ and at voltage $V$ are

\begin{equation}
I_e = GV + B \delta T,
\end{equation}

\begin{equation}
I_h = \Gamma V + \Xi \delta T.
\end{equation}

The off-diagonal coefficients, $B$ and $\Gamma$, are related by Onsager’s principle: $\Gamma = -TB$.

To the leading order in $(E_F/\tau)^{-1}$, the electron–electron interaction does not affect the fluctuations of transport coefficients at low temperature ($\tau$ is the mean elastic scattering time)\(^15\); in addition inelastic scattering due to interactions at finite temperature may be neglected in the mesoscopic regime. Interactions in disordered metals do affect the average electric and thermal conductances and can lead to a violation of the WF law\(^16,17\); however this effect does not have magnetic flux sensitivity and its temperature dependence is different from that of the mesoscopic violation studied here.

Neglecting the interaction effects, the thermoelectric coefficients can all be expressed in terms of integrals over $G(\varepsilon)$, where the $T = 0$ conductance at energy $\varepsilon$ is given by the Landauer-Büttiker formula $G(\varepsilon) = 2G_0 \sum_{\alpha, \beta} |t_{\alpha\beta}(\varepsilon)|^2$ and $t_{\alpha\beta}(\varepsilon)$ is the transmission amplitude for conduction channels $\alpha, \beta$. Defining the energy moments of the conductance $G(\varepsilon)$ at temperature $T$ and chemical potential $\mu$ by

\begin{equation}
G^{(n)}(T) = - \int_{-\infty}^{\infty} J_n(\varepsilon) d\varepsilon,
\end{equation}

PACS number(s): 73.23.–b, 72.15.Eb, 73.63.Kv
as for the bulk conductivities:

FIG. 1. (Color online) Upper panel shows the thermal weight functions for the electrical current, \(I_e\), and for the heat current, \(I_h\). For constant electron transmissivity \(-G(e)\) on the scale of \(k_B T\), the ratio of areas below these functions leads to the WF law, which thus always holds as \(T \to 0\). However, if \(\delta G(e)\) fluctuates on the scale of \(E_c \sim k_B T\) (lower panel), then \(\delta G(e)\) is unequally weighted for \(I_e\) and \(I_h\) and sample-specific corrections to the WF law appear.

\[
J_n(e) = G(e) \frac{(e - \mu)^n}{(k_B T)^n} \frac{df}{de},
\]

one finds that \(G = G(0), B = -(k_B e) G(1)\), and \(\Xi = (k_B e)^2 T G(2)\). The thermal conductance \(G_h = I_h / \delta T\), measured when \(I_e = 0\). From Eq. (1) we have \(G_h = \Xi - 1/B GT\). The WF law has the same form for these conductance coefficients as for the bulk conductivities: \(G_h / GT = I_h\).

If \(G(e)\) is constant on scales much greater than \(k_B T\), then the thermal conductance \(G_h\) obeys the WF law to very high accuracy. First, if \(G(e)\) is constant and hence equal for electrons and holes within \(k_B T\) of the Fermi energy, then no net electrical current flows between the two reservoirs under a thermal gradient and the thermopower is zero: \(\Gamma = -T B = 0\).

Thermal current does flow since the colder reservoir receives more electrons with energy \(e - \mu > 0\) and holes with energy \(e - \mu < 0\); this flux is given by setting \(G(e) = G(\mu) = G_\mu\), leading immediately to \(G(2) = (\pi^2 / 3) G_\mu\) and \(G_h / GT = G = \Xi / G = l_0 / T\). Thus, the WF law does hold as \(T \to 0\) for mesoscopic conductors; fluctuations in both thermal and electrical conductances maintain a fixed ratio given by the WF law.

If \(G(e)\) does vary on the scale of \(k_B T\), then one cannot approximate \(G(e)\) by \(G_\mu\), the thermal and electrical currents have different weighting factors (see Fig. 1), and their ratio is no longer fixed at the WF value. Thus mesoscopic conductors will begin to violate the WF law at temperatures which are on the scale of variation of \(G(e)\). This scale is \(E_c = h / \tau_i\), where \(\tau_i\) is the typical transit time between the reservoirs and depends on the geometry of the conductor.\(^5\) Since the mesoscopic conductance fluctuates by \(\delta G \sim e^2 / h\) on this scale, we can immediately estimate the maximum size of the violation of the WF law. Define the Lorenz ratio to be

\[
l = \frac{G_h}{GT} = \frac{\Xi}{GT} - \frac{\Gamma B}{TG^2},
\]

where \(G = G_\mu + \delta G(T)\) and \(\Xi = l_0 T G_\mu + \delta \Xi(T)\). The fluctuating contributions \(\delta G(T), \delta \Xi(T)\) are \(\sim g^{-1}\); therefore the fluctuating part of the first term in Eq. (3) is \(\delta \Xi / G = l_0 \left[ \delta \Xi / l_0 G_\mu - \delta G / G_\mu \right] \sim g^{-1}\). In contrast, the thermopower coefficients \(\Gamma, B\) are zero in leading order and only have a contribution from the mesoscopic fluctuations;\(^8,9,11\) therefore the fluctuating part of the second term in Eq. (3) is \(\Gamma B / G^2 \sim g^{-2}\) and the thermopower fluctuations do not contribute to the violation of the WF law at leading order. Thus the fluctuations \(l_0 \eta\) in the Lorenz ratio \(l\) are given by

\[
l = l_0 (1 + \eta) = \frac{\Xi}{GT}, \quad \eta = \frac{1}{G_\mu} \left[ \frac{\delta \Xi}{l_0 T} - \delta G \right].
\]

The standard deviation of the dimensionless quantity \(\eta\) gives us the typical violation of the WF law. Before averaging for \(k_B T \ll E_c\) we can expand \(G(e)\) in Eq. (2) around \(e = \mu\) to order \((e - \mu)^2\). The zeroth order yields the WF law, the first order vanishes by symmetry, and the second order will give a correction \(- (k_B T)^2 G(\mu) / G_\mu\), which for a mesoscopic sample will be \(\sim (k_B T / E_c)^2 g^{-1}\). Hence the deviation from the WF law will rise quadratically for \(k_B T \ll E_c\) and become \(\sim g^{-1}\) at \(k_B T \sim E_c\). When \(k_B T \approx E_c\), the typical violation will again decrease as the random contributions from energies \(e\) begin to self-average over the window \(k_B T\).

The quantitative behavior of the fluctuations can be obtained from the variance of \(\eta\), which is determined by the zero temperature conductance correlation functions \(K((e - e') / E_c) = \langle \delta G(e) \delta G(e') \rangle / G_0^2\) as

\[
\text{var}(\eta) = \frac{G_0^2}{(G_\mu)^2} \left[ 9 C_{22} \frac{9 C_{20}}{\pi^4} - 6 C_{20} \frac{C_{00}}{\pi^2} + C_{00} \right] = \frac{f^2(T, E_c)}{g^2},
\]

where the coefficients \(C_{nm} = \langle \delta G(n) \delta G(m) \rangle / G_0^2\) refer to integrals of the form

\[
C_{nm} = \int_{-\infty}^{\infty} de d e' \frac{df \, df}{d e \, d e'} \frac{(e - \mu)^n (e' - \mu)^m}{(k_B T)^{n+m}} K \left[ \frac{e - e'}{E_c} \right].
\]

As already noted, the typical value of the violation of the WF law is \(\text{rms}(\eta) = f(T, E_c) g\); the function \(f(T, E_c)\) is plotted for the geometry of a quasi-one-dimensional metallic wire and an open quantum dot in Fig. 2. As expected, the maximum of \(f(T, E_c)\) occurs at \(k_B T \sim E_c\) and \(f(T, E_c)\) vanishes for both...
For a diffusive mesoscopic system (i.e., a system with the elastic mean free path shorter than all sample dimensions) the conductance correlation function $K(\Delta e/E_c)$ has been calculated by impurity-averaged perturbation theory\textsuperscript{6,7} and can be expressed in terms of sums over the eigenvalues of the diffusion and cooperon propagators.\textsuperscript{18,19} For the case of a disordered quasi-one-dimensional wire of length $L$ with diffusion coefficient $D$, we have $E_c = D/L^2$ and

$$K(\xi, x) = \frac{3}{8} \frac{2x^2}{(\xi^2 + x^2)^2}, \quad E_c = D/L^2$$

(7)

where the parameter $\beta = 1$ in the presence of time-reversal symmetry and $\beta = 2$ in its absence, and we have included spin degeneracy. Time-reversal symmetry is effectively broken by a magnetic field comparable to a flux $\Phi_0 = h/e$ through the wire, typically rather weak fields. Experiments that rely on varying magnetic field to observe fluctuations will correspond to the case $\beta = 2$. The function $f(T, E_c)$ giving rms $\eta$ for a wire is plotted as the solid line in Fig. 2; it has the asymptotes

$$f(T, E_c) = \frac{64}{5} \sqrt{\frac{7}{3}} \left[ \frac{k_BT}{E_c} \right]^2, \quad k_BT \ll E_c,$$

(8a)

$$f(T, E_c) = \frac{4}{3\pi} \sqrt{\frac{4\pi^2 - 30}{5\pi}} \sqrt{\frac{E_c}{k_BT}}, \quad k_BT \gg E_c. \quad \text{(8b)}$$

The maximum of $f(T, E_c)$ is $f_{\text{max}}(T, E_c) = 0.23$ at $k_BT_{\text{max}} = 0.5E_c$ leading to a violation of the WF law $-0.23/g$. This expression describes both micron scale and nano scale metallic wires as well as semiconducting quantum wires in the diffusive regime for $g \gg 1$. For such systems the dimensionless conductance $g$ can vary between $10^5-10^9$. When $g$ approaches unity it will be necessary to include the thermopower corrections to the WF law as well and the violation, while order unity, will not be quantitatively described by $f(T, E_c)$.

B. Aharonov-Bohm oscillations

In order to make the mesoscopic deviation from the WF law more easily measurable, it will be convenient to fabricate ring structures similar to those used to first measure the mesoscopic $h/e$-periodic Aharonov-Bohm (AB) effect in normal metals.\textsuperscript{20,21} In this case the mesoscopic quantum corrections to the conductance are the only terms that give rise to oscillations of the conductance with period $h/e$ and these terms are relatively easy to isolate by Fourier transforming the measured behavior of $G(\Phi)$ and $G_0(\Phi) = \Xi(\Phi)$, where $\Phi = B$ is the magnetic flux through the ring in magnetic field $B$. We consider then the ratio of harmonics of the AB oscillations at frequency $k/\Phi_0$, $k = 1, 2, \ldots$ in $G(\Phi)$ and $\Xi(\Phi)$. For $k_BT \ll E_c$ we have the simple result that $\partial G(\Phi) / \partial \Phi = G_0(\Phi)$ and $\partial \Xi(\Phi) / \partial \Phi = \Xi(\Phi)$, hence $\partial G(\Phi) / \partial \Phi = G_0(\Phi) = l_0T$ for all $\Phi$. The AB oscillations are perfectly in phase and their ratio need not be the Lorenz number. To quantify their relationship we calculate the harmonics of the conductance and heat conductance correlation functions (in flux) for such a ring. Let $F(\Delta \Phi) = \langle \delta G(\Phi) \delta G(\Phi + \Delta \Phi) \rangle$ and $F(\Delta \Phi) = \langle \delta \Xi(\Phi) \delta \Xi(\Phi + \Delta \Phi) \rangle$: Neglecting the flux through the wires making up the ring (i.e., including only the flux through the hole) these functions are periodic with fundamental frequency $\Phi_0$ and can be represented in terms of their harmonics $F^{(k)}_{G, \Xi}$

$$F_{G, \Xi}(\Delta \Phi) = \alpha \sum_{k=0}^{\infty} F^{(k)}_{G, \Xi} \cos \left( \frac{2\pi k d \Phi(\Delta \Phi)}{\Phi_0} \right),$$

(9)

where $\alpha$ is geometry-dependent factor. As in Eq. (7), the relevant correlation functions can be expressed as sums where for the ring the integers in the sum appear only in the combination $m = -\Delta \Phi/\Phi_0$ (leading to an obvious periodicity in $\Phi_0$). It is convenient in this case to rewrite the sum using the Poisson summation formula where the integration variable is shifted to $\phi = m - \Delta \Phi/\Phi_0$. This yields a relatively simple formula for the harmonics $F^{(k)}_G = G_0^{(k)} F^{(k)}_R$ of the electrical conductance and for the harmonics $F^{(k)}_{\Xi} = (G_0^{(k)})^2 F^{(k)}_R$ of the thermal conductance. Here

$$F^{(k)}_{nm} = \int_{-\infty}^{\infty} d\phi d\epsilon \frac{df}{de} \frac{d^2f}{de^2} \left( \frac{e - \mu}{k_BT} \right)^m \times \int_{-\infty}^{\infty} d\phi \cos(2\pi k\phi) K(\frac{\phi^2 + \gamma - e^2}{E_R^2 - E_R^2})$$

(10)

with kernel $K(\xi, x)$ defined by Eq. (7), $E_R = D/R^2$ is inversely proportional to the electron diffusion time along a circumference of the ring of radius $R$, and $\gamma$ takes into account electron escape from the ring through the leads and other phase relaxation rates, such as electron-electron or electron-phonon dephasing rates.

Performing the integrations in Eq. (10), we find that the ratio of the harmonics of $\Xi$ to $G$ decreases from the WF value monotonically with increasing temperatures until it saturates at $k_BT \approx E_R$, $\gamma$, to the value

$$\frac{1}{T^2} \frac{F^{(k)}_{n,m}}{F^{(k)}_G} = \frac{21}{5 \pi^2} - \frac{180}{5 \pi^2} l_0^2 = 0.55 l_0^2.$$ 

(11)

In this temperature regime the conductance and heat conductance AB oscillations will appear uncorrelated and their ratio will randomly vary at each value of magnetic flux $\Phi$; it is only the ratio of their variances (or harmonics) averaged over magnetic fields which will saturate to a constant value. This saturation value will be different by roughly a factor of 0.55.
from the value expected from the WF law. The reason that the saturation value is less than the WF value when \( k_B T > E_c \) is that the conductance fluctuations are determined by transmission fluctuations within \( k_B T \) of the Fermi level, while the thermal conductance fluctuations are determined by transmission fluctuations in two regions of width \( k_B T \) displaced from the Fermi level by \( \sim k_B T \), see Fig. 1. Hence the contributions from different energies to the thermal conductance fluctuations are less correlated and tend to cancel each other more than the contributions to the electrical conductance fluctuations. We plot the ratio \( F_{\Xi}^{(k)} / F_G^{(k)} \) as a function of \( k_B T / E_R \) for several values of \( \gamma \) in Fig. 3.

### C. Open quantum dots

If we consider semiconducting systems, the above calculations also apply and since \( g \) is typically much smaller one expects large violations of the WF law, although in general the WF law is not well-satisfied in semiconductors so the novelty is less than in metals. Semiconducting quantum dots exhibit large aperiodic thermopower fluctuations as a function of magnetic field\(^{13}\); these have been treated theoretically by Van Langen et al.\(^{11}\). The behavior of the Lorenz number for this case was not studied either experimentally or theoretically. As long as the number of open channels \( N \gg 1 \), our Eq. (5) for the variance of \( \eta \) still applies with the only change being the replacement of Eq. (7) for the conductance energy correlation function by the appropriate function for an open quantum dot. If we assume the quantum dot junction generates chaotic scattering, then the S-matrix of the system will be described approximately by the Dyson ensembles of random matrix theory and the energy correlation function \( K_{\rm qd}(\Delta E/E_c) = (N^2/N^2_{\text{ch}}) (1 + \Delta E/E_c)^{-\delta_1} \), where \( E_c = N_{\text{ch}} \delta_1 / (2 \pi) \), \( N_{\text{ch}} \), \( N_i \) are the number of incoming channels in the left and right leads of the junction, \( N_{\text{ch}} = N_l + N_r \), and \( \delta_1 \) is the mean level spacing of electron states in the dot.\(^{22}\) Substituting \( K_{\rm qd}(\delta) \) into Eq. (6), we calculate \( \var(\eta) = f_{\text{qd}}^{(k)}(T, E_c) / g^2 \) with \( g = 2N_i/N_{\text{ch}} \) from Eq. (5). \( f_{\text{qd}}^{(k)}(T, E_c) \) has the following asymptotic forms:

\[
f_{\text{qd}}^{(k)} = \frac{16 \pi^2}{5} \left[ \frac{2N_i N_l}{N_{\text{ch}}^2} \left( \frac{k_B T}{E_c} \right)^2 \right], \quad k_B T < E_c, \quad (12a)
\]

\[
f_{\text{qd}}^{(k)} = \sqrt{\frac{2N_i N_l}{N_{\text{ch}}^2}} \left( \frac{k_B T}{E_c} \right)^2, \quad k_B T \gg E_c, \quad (12b)
\]

### III. THERMOPOWER

For completeness we make a few brief comments about the thermopower coefficient, which has been treated in Refs. 8, 9 for the case of a disordered wire and in Ref. 11 for the case of a chaotic quantum dot. The thermopower \( Q = -B / G \) is the coefficient of the voltage induced by a temperature difference when no electrical current flows, \( I_c = 0 \). To leading order in the Sommerfeld expansion \( Q = 0 \) and at first order \( Q \approx (k_B T / e) G_0 / G_\mu - (k_B T / E_c) \) for a macroscopic conductor. For a mesoscopic conductor \( G_\mu / G_\mu - (1 / g E_c) \) and the thermopower fluctuates in sign and for \( k_B T < E_c \) is enhanced by a factor \( (E_c / E_c) g^{-1} \) that is typically several orders of magnitude. The fluctuations of \( Q \) to the lowest order in \( 1 / g \) are determined by fluctuations of \( B \). The latter can be calculated from Eq. (6) for \( C_{11} \):

\[
\var(B) = \left( \frac{k_B G_0}{e} \right)^2 C_{11} = \left( \frac{k_B G_0}{e} \right)^2 h^2(T, E_c). \quad (13)
\]

The behavior of rms(\( B \))=\( (k_B G_0 / e) h(T, E_c) \) as a function of \( k_B T / E_c \) is similar but not identical to that of \( \var(\eta) \), increasing linearly with \( T \) for \( k_B T \ll E_c \) and then decaying as \( T^{-1/2} \) for \( k_B T \gg E_c \); see Fig. 4. For diffusive wires, \( h(T, E_c) \) was calculated in Ref. 9. Here we present the low and high temperature asymptotes of \( h(T, E_c) \):

\[
h(T, E_c) = \frac{2}{3} \sqrt{10 \zeta(8)} \left( \frac{k_B T}{E_c} \right), \quad k_B T \ll E_c, \quad (14a)
\]

\[
h(T, E_c) = 2 \left( \frac{k_B T}{E_c} \right)^{1/2}, \quad k_B T \gg E_c, \quad (14b)
\]
with $E_c = D/L^2$. The maximum of $h(T, E_c)$ is $h_{\text{max}} = 0.17$ at $k_B T = 0.37 E_c$. For geometry of an open quantum dot, $E_c = N_{\text{ch}} \theta_0 / (2 \pi)$ and the asymptotes are

$$h_{\text{qd}}(T, E_c) = \sqrt{\frac{\pi^2 - 6}{27 \pi}} \sqrt{\frac{E_c}{k_B T}}, \quad k_B T \gg E_c, \quad (14b)$$

The maximum of $h = 0.66 N_{\text{ch}} / h_{\text{ch}}^2$ occurs at $k_B T = 0.49 E_c$. The low temperature asymptote, Eq. (15a), was previously found in Ref. 11.

The maximum fluctuations in thermopower are $Q_{\text{max}} \sim (k_B / e) g^{-1}$ at $k_B T \sim E_c$. The thermopower corrections to the thermal conductance $G_h$ are always smaller than the direct quantum correction by a factor $g^{-1}$ and therefore only play a significant role in the violation of the WF law when $g$ approaches unity.

**IV. CONCLUSIONS**

In conclusion, we evaluated the variance of the ratio of the heat and electric conductances in mesoscopic systems. We showed that this ratio does not fluctuate as $T \to 0$ and exactly satisfies the Wiedemann-Franz law, but fluctuates with a finite variance for nonzero $T$ and is a nonmonotonic function of temperature with a maximum at temperature equal to the Thouless energy. The ratio of the $e/h$ harmonic of the heat and electric conductance correlation functions in an Aharonov-Bohm geometry satisfies the Wiedemann-Franz law only at low temperatures; at high temperatures their ratio becomes $0.55 \theta_0$.

**ACKNOWLEDGMENTS**

We thank Venkat Chandrasekhar for discussion of his recent experiments. This work was supported by the W. M. Keck Foundation and by NSF Materials Theory Grant No. DMR-0408638.