Thermoelectric coefficients and the figure of merit for large open quantum dots

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June 14, 2018

Abstract

We consider the thermoelectric response of chaotic or disordered quantum dots in the limit of phase-coherent transport, statistically described by random matrix theory. We calculate the full distribution of the thermoelectric coefficients (Seebeck $S$ and Peltier $\Pi$), and the thermoelectric figure of merit $ZT$, for large open dots at arbitrary temperature and external magnetic field, when the number of lead modes $N$ is large. Our results show that the thermoelectric coefficients and $ZT$ are maximal when the temperature is half the Thouless energy, and the magnetic field is negligible. We find that the thermoelectric coefficients and $ZT$ are small, but they exhibit a type of universality, in the sense that they do not depend on the asymmetry between the left and right leads.

Contents

1 Introduction 2
  1.1 Works on similar systems in different regimes 3

2 Thermoelectric coefficients and figure of merit 4
  2.1 Evaluating the averages in Eqs. (7,8) 5
  2.2 Typical magnitude of the thermoelectric effects 7
  2.3 Average figure of merit 8

3 Universality of the Seebeck coefficient and figure of merit 9

4 Full probability distributions 9
  4.1 Full distribution of the thermoelectric coefficients 11
  4.2 Full distribution of the figure of merit 11

5 Diagrammatics for open chaotic or disordered dots 11
  5.1 Diagrams for $\langle T(E) \rangle$ 13
  5.2 Diagrams for $\langle \delta T(E_1) \delta T(E_2) \rangle$ 14
1 Introduction

There has long been interest in the thermoelectric response of nanostructures [3–6]. However, research in this field was restricted by the absence of good thermometry techniques at the nanoscale, which made it extremely hard to quantify heat flows. In recent years, numerous such thermometry techniques have been developed, leading to a renewed interest in thermal transport and thermoelectric effects at the nanoscale, see for example Refs. [7,8] and references therein.

In many cases, the objective is to maximize the thermoelectric response for applications, such as efficient new power sources or refrigerators, or for the recovery of useful power from waste heat. However, at a more fundamental level, the measurement of a thermoelectric response is a very interesting probe of the physics of a nanostructure. It always gives us different information from the measurement of the nanostructure’s electrical conductance. At a hand waving level, one can say that the thermoelectric response tells us about the difference between the dynamics of charge carriers above and below the chemical potential, when the electrical conductance only tell us about the sum of the two [7]. It is important to develop good quantitative models of the thermoelectric response of all kinds of nanostructures, to help us use the thermoelectric response as a quantitative probe of the physics of a nanostructure. In this context, we should maintain our interest in modelling nanoscale systems whose thermoelectric response is small, as well as in modelling those whose response is large.

Chaotic or disordered quantum dots have random properties whose statistics are described by random matrix theory. In particular, such dots have a spread of Seebeck coefficients, $S$, centred on zero, which means the average of the Seebeck coefficient over realizations of the disorder or the chaos, $\langle S \rangle$, is zero. The Peltier coefficient in such a two-terminal dot is $\Pi = TS$ for arbitrary external magnetic field [5, 9], so it is also zero on average. However, in such a situation, if one takes a single typical dot, it will have Seebeck and Peltier coefficients of random sign but of non-zero magnitude. The typical value of such coefficients will be

$$S_{\text{typical}} \simeq \pm \sqrt{\langle S^2 \rangle} \quad \text{with} \quad \Pi_{\text{typical}} = TS_{\text{typical}}.$$ (1)

The dimensionless figure of merit $ZT$ which measures the system’s efficiency as a thermoelectric heat engine (see table 1 in Ref. [7]), or its efficiency as a refrigerator, is

$$ZT = \frac{GS^2T}{K},$$ (2)

for temperature $T$, electrical conductivity $G$ and thermal conductivity $K$. Since this contains $S^2$, and we know both $G$ and $K$ must be positive, we see that this will not average to zero.
It would be useful to know both $S_{\text{typical}}$ and $\langle ZT \rangle$ as a function of system parameters and temperature. Even better would be to have the full distribution of $ZT$, so one could answer questions such as, what percentage of samples will have a $ZT$ greater than a given value.

This work treats such a problem in the simplest case, spinless electrons flowing through a large open quantum dots, where the dot is coupled to many reservoir modes, $N \gg 1$. This implies that the level broadening in the dot is of order $N$ times the dot’s level spacing, so the transmission though the dot is only weakly energy dependent. Since high efficiencies rely on good energy filtering, it should be no surprise that this limit has a $ZT$ much less than one.

The seminal work on this subject was that of van Langen, Silvestrov, and Beenakker [10], which contains a plethora of results on the Seebeck coefficient in coherent transport through disorder wires and dots. Here, we revisit their result for large $N$, stated in the conclusions of Ref. [10], which says that the typical magnitude of the Seebeck coefficient $S_{\text{typical}}$ is small (in units of $k_B/e$) but grows with increasing temperature. It is clear that the result was only for the low temperature limit (temperature much smaller than the Thouless energy), and it is not hard to guess that $S_{\text{typical}}$ will not continue to grow with temperature for larger temperatures. However, it raises the question; what value of temperature maximizes the thermoelectric response, and how big is this thermoelectric response?

This work answers this question, making the following modest but four-fold contribution to the subject.

(i) We extend the result in Ref. [10] to arbitrary temperatures and arbitrary magnetic fields (as we treat spinless electrons, spin-orbit coupling is not present). This show that the thermoelectric coefficients (Seebeck and Peltier effects) are maximized when $k_B T$ is half the Thouless energy, $E_{\text{Th}}$, and the external magnetic field is negligible.

(ii) This maximum also corresponds to the maximal thermoelectric figure of merit, $ZT$. Not unexpectedly, it remains much smaller than one even at its maximum.

(iii) We recover Ref. [10]’s result that the distribution of $S$ is Gaussian, and show that this implies that the distribution of $ZT$ is an exponentially decaying function of $ZT$, with a square-root divergence at small $ZT$.

(iv) We show that both $S$ and $ZT$ have a type of universality, in the sense that they do not depend on the asymmetry in the number of modes in the left and right leads (even though they depend on the total number of lead modes, $N$). So for example, $S$ and $ZT$ have exactly the same average value and exactly the same distribution for a dot with highly asymmetric leads with $N_L = 100$ and $N_R = 300$, as for a dot with symmetric leads with $N_L = N_R = 200$.

In all cases, we explain how to derive these results (the results in Ref. [10] were mainly stated without derivation) using a diagrammatic method that works for chaotic or disordered systems that obey random matrix theory.

1.1 Works on similar systems in different regimes

Ref. [10] discussed the low temperature limit for both the limit of large $N$ and small $N$, with Refs. [11,12] going further with small $N$. Ref. [33] extended these low temperature results to systems with decoherence and relaxation, as modelled by a voltage probe. Ref. [34] is another interesting recent work for small $N$, which considers the band-edge of a system described.
Figure 1: The systems we consider in this work are those described by random matrix theory, this could be (a) a disordered system or (b) a chaotic system (such as a Sinai billiard). In both cases the system is coupled to two reservoirs (left and right) through leads with $N_L$ and $N_R$ modes respectively. The number of lead modes $N_i$ for a lead of width $W_i$ is given above Eq. (12b). We define $N = N_L + N_R$, and consider the properties of the ensemble of such systems for $N \gg 1$, as modelled by an ensemble of random matrices. In the case of the disordered system, this ensemble corresponds to the ensemble of systems with the disorder in different positions. In the case of chaotic systems, this ensemble corresponds to an ensemble of shapes of the potential; for the Sinai billiard, such an ensemble can be found by varying the radius $R$ over a range much larger than the particle wavelength but much smaller than the system size.

by a random matrix, where the levels are very sparse, so can be modelled by just two such levels, and considers the limit where the thermal conductance is dominated by phonons, so $ZT = GS^2/K_{\text{phonon}}$, and the statistics of $ZT$ are entirely determined by the statistics of $GS^2$. Another work which considered open quantum dots (in the large $N$ limit) is Ref. [42], however this mainly considers the non-zero value of $\langle S \rangle$ that is induced by a superconducting loop threaded by a flux.

While it is not the subject of this work, it is worth mentioning a significant activity the thermoelectric response of disordered one-dimensional wires, both in the coherent transport regime [10,35–37], and the variable range hopping regime [36,38–41].

2 Thermoelectric coefficients and figure of merit

We consider systems of the types shown in Fig. 1 in the linear response regime, where the thermoelectric transport through the system can be written in terms of integrals over the transmission function $T(E)$ via the Landauer scattering theory [1–5]; for a review see Chapters 4 and 5 of Ref. [7]. One can write the electrical conductivity $G$, thermal conductivity $K$, Seebeck coefficient $S$, and Peltier coefficient $\Pi$ in terms of coefficients of the Onsager matrix, which can then be written in term of integrals over the transmission function (see e.g. section 5.2 of Ref. [7]). Then

$$G = e^2 I_0,$$

$$K = \frac{1}{T} \left( I_2 - \frac{I_1^2}{I_0} \right),$$

$$S = \frac{1}{eT} \frac{I_1}{I_0},$$

$$\Pi = \frac{1}{e} \frac{I_1}{I_0},$$

(3)
with the integral
\[ I_n \equiv \int_{-\infty}^{\infty} \frac{dE}{\hbar} (E - \mu)^n \mathcal{T}(E, \mathbf{B}) \left[ -f'(E) \right], \tag{5a} \]
where \( \mu \) is the chemical potential, and \( f'(E) \) is the derivation of the Fermi function with respect to energy, so
\[ f'(E) = -\frac{1}{4k_BT \cosh^2 \left[ E/(2k_BT) \right]} \]. \tag{5b}

The Seebeck coefficient of such a dot is zero on average because its sign is random, however a typical system will have a Seebeck coefficient of order \( \pm \sqrt{\langle S^2 \rangle} \). Ref. \[10\] already gave a result for \( \langle S^2 \rangle \) in the large \( N \) limit (see the Conclusions at the end of Ref. \[10\]), which grows like \((k_BT/E_{Th})^2\). It is natural to guess that this result can only hold for small \( T \), and the quadratic growth must stop at some value of \( T \). Here we ask, what is the \( T \)-dependence at larger \( T \), and how big can the typical Seebeck coefficient become? At the same time, we ask what is the average value of the figure of merit \( ZT \) as a function of temperature? For \( ZT \), combining Eqs. (2-4), one finds that
\[ ZT = \frac{I_1^2}{I_2 I_0 - I_1^2}. \tag{6} \]

One immediately sees from Eqs. (4,6) that to average \( S^2 \) or \( ZT \) over realizations of the chaos or disorder, one is required to take averages of products and ratios of integrals containing transmission functions. In general, this is a highly difficult technical problem. However, in the limit of \( N \gg 1 \), the situation is greatly simplified by the fact that \( I_0 \) and \( I_2 \) have fluctuations much smaller than their average. Writing \( I_0 = \langle I_0 \rangle + \delta I_0 \) and \( I_2 = \langle I_2 \rangle + \delta I_2 \), and counting powers of \( N \) in the manner described later in this article (or in Ref. \[31\]), one finds that \( \langle I_0 \rangle \sim \langle I_2 \rangle \sim N \) while \( I_1 \sim \delta I_0 \sim \delta I_2 \sim 1 \). Thus
\[ \langle S^2 \rangle = \frac{1}{e^2 T^2} \frac{\langle I_1^2 \rangle}{\langle I_0 \rangle^2} \left[ 1 + \mathcal{O}(1/N) \right] \], \tag{7} \]
\[ \langle ZT \rangle = \frac{\langle I_1^2 \rangle}{\langle I_2 \rangle \langle I_0 \rangle} \left[ 1 + \mathcal{O}(1/N) \right]. \tag{8} \]

2.1 Evaluating the averages in Eqs. (7,8)

We will treat the problem of finding averages of \( I_0 \), \( I_1 \) and \( I_2 \) in the limit of \( N \gg 1 \) using the diagrammatic rules, which were derived from a semiclassical treatment of trajectories in a chaotic cavity, and shown to coincide exactly with the results of random matrix theory \[17, 28, 29\]. This work will use two results of this diagrammatic method derived in Refs. \[13, 18\]. The first result, whose derivation we outline in Section 5.2 is
\[ \langle \mathcal{T}(E) \rangle = \frac{N_L N_R}{N} \left[ 1 + \mathcal{O}(1/N) \right], \tag{9} \]
where \( N = N_L + N_R \) is the total number of lead modes. Defining the deviation of the transmission from its average value as,
\[ \delta \mathcal{T}(E) = \mathcal{T}(E) - \langle \mathcal{T}(E) \rangle, \tag{10} \]
the second result of the diagrammatic method in Section 5.2 is
\[ \langle \delta \mathcal{J}(E_1) \delta \mathcal{J}(E_2) \rangle = \frac{N_L^2 N_R^2}{N^4} \left\{ \left( 1 + \frac{B^2}{B_c^2} + \frac{\Delta E^2}{E_{\text{Th}}^2} \right)^{-1} + \left( 1 + \frac{\Delta E^2}{E_{\text{Th}}^2} \right)^{-1} \right\} \left[ 1 + O\left( \frac{1}{N} \right) \right]. \] (11)
where for compactness we define \( \Delta E = E_2 - E_1 \). The two parameters in \( \langle \delta \mathcal{J}(E_1) \delta \mathcal{J}(E_2) \rangle \) are the Thouless energy, \( E_{\text{Th}} \), and the crossover field, \( B_c \). The Thouless energy is defined as
\[ E_{\text{Th}} = \hbar/\tau_D, \] (12a)
with \( \tau_D \) being the average time a particle spends in the dot. For a \( d \)-dimensional dot of typical volume \( L^d \), and with lead \( i \) having width \( W_i \) and so carrying \( N_i \sim (p_F W_i / \hbar)^{d-1} \) modes, one has
\[ E_{\text{Th}} \sim \frac{\hbar v_F}{L} \left( W_L^{d-1} + W_R^{d-1} \right) \sim \frac{\hbar v_F N}{L} \left[ \frac{h}{p_F L} \right]^{d-1}, \] (12b)
where \( v_F = p_F / m \) is the Fermi velocity and we drop many factors of order one. This Thouless energy can be thought of as the broadening of dot levels due to the finite probability of escape into the leads; it is of order \( N \) times the dot level-spacing. Thus for large \( N \), the dot has a smooth and almost constant density of states. The crossover field, \( B_c \), is the external magnetic field which induces the crossover from the time-reversal symmetric system to the one with broken time-reversal symmetry. Physically, \( B = B_c \) corresponds to the field where a typical trajectory through the system encloses one flux quantum. For a system of area \( A \sim L^2 \), which an electron with velocity \( v_F \) crosses in a time \( \tau_0 \sim L / v_F \), one has
\[ B_c \sim (h/eA)(\tau_0/\tau_D)^{1/2}, \] (13)
see e.g. Section VE of Ref. [30] or Section IIB4 of Ref. [31].

Since \( \langle \mathcal{J}(E) \rangle \) is energy independent, the integrals of it over \( E \) are known for \( n = 0, 1, 2 \). Hence,
\[ \langle I_n \rangle = \frac{1}{\hbar} \frac{N_L N_R}{N} \times \left\{ \begin{array}{ll} 1 & \quad \text{for } n = 0, \\ 0 & \quad \text{for } n = 1, \\ \pi^2 k_B^2 T^2 / 3 & \quad \text{for } n = 2. \end{array} \right. \] (14)
Next, we note that
\[ \langle I_1^2 \rangle = \int dE_1 dE_2 \frac{(E_1 - \mu)(E_2 - \mu)}{\hbar^2} \langle \mathcal{J}(E_1) \mathcal{J}(E_2) \rangle f'(E_1) f'(E_2), \] (15)
so using Eq. (11) and defining \( y_i = (E_i - \mu) / (k_B T) \), we find that
\[ \langle I_1^2 \rangle = \frac{N_L^2 N_R^2}{N^4} \frac{k_B^2 T^2}{\hbar^2} \left[ F \left( k_B T \frac{E_{\text{Th}}}{E_{\text{Th}}} - 1 \right) + F \left( k_B T \frac{E_{\text{Th}}}{E_{\text{Th}}} - 1 + \frac{B^2}{B_c^2} \right) \right], \] (16a)
where to lowest order in \( 1/N \),
\[ F(x, b) = \frac{1}{16} \int \frac{dy_1 dy_2}{b + (y_1 - y_2)^2 x^2} \frac{1}{\cosh^2[y_1/2] \cosh^2[y_2/2]}. \] (16b)
Figure 2: Here we plot $F(x, b)$ given in Eq. (16b) versus $x$, for various values of $b$ (where we are only interested in $b \geq 1$). We see that the function is peaked at $x$ of order one (typically between 0.5 and 1). The function goes like $x^2$ for small $x$ (on a scale almost too small to see here), while it goes like $1/x$ for large $x$.

This function is plotted in Fig. 2, it is non-monotonic with a maximum at $x \simeq 0.5, b = 1$ (given that we are only interested in $b \geq 1$). This tells us that the maximum $\langle I^2 \rangle$ occurs when $k_B T \simeq E_{Th}/2$. Even without this plot, the following arguments tell us that $F(x, b)$ goes like $x^2$ at small $x$, and decays like $1/x$ at large $x$, which implies it has a peak when $x$ is of order one for any $b \geq 1$.

To get the small $x$ behaviour of $F(x, b)$, it is sufficient to note that $F(0, b) = 0$, because the integrand is an odd function of $y_1$ and $y_2$. Then for small $x$, one has $F(x) \sim x^2$, because the leading term in the expansion of $[b + (y_1 - y_2)^2 x^2]^{-1}$ is of order $x^2$. To get the large $x$ behaviour of $F(x, b)$, one can use the hand-waving argument that the integrand is of order $y_1 y_2$ in a rectangle given by $-2 < (y_1 + y_2) < 2$ and $-1/x < y_1 - y_2 < 1/x$, and is small enough to neglect outside this rectangle. One then goes to coordinates $z_\pm = y_1 \pm y_2$, so $y_1 y_2 \sim z_+^2 - z_-^2$, for which the integral takes the form $\int_{-2}^2 dz_+ \int_{-1/x}^{1/x} dz_- (z_+^2 - z_-^2) \sim 1/x$ (dropping all prefactors of order one).

### 2.2 Typical magnitude of the thermoelectric effects

The Seebeck coefficient of such a dot is zero on average because its sign is random, however a typical dot will have a Seebeck coefficient given in Eq. (1). Ref. [10] already gave a result for $\langle S^2 \rangle$ in the large $N$ limit (see the Conclusions at the end of Ref. [10]), which grows like $(k_B T/E_{Th})^2$. It is natural to guess that this result can only hold for small $T$, and the quadratic growth must stop at some value of $T$. Here we ask, what is the $T$-dependence for arbitrary $T$, and how big can the typical Seebeck coefficient become?

Substituting the averages in Section 2.1 into Eq. (7), we find that

$$\langle S^2 \rangle = \frac{k_B^2}{e^2} \frac{1}{N^2} \left[ F\left(\frac{k_B T}{E_{Th}}, 1\right) + F\left(\frac{k_B T}{E_{Th}}, 1 + \frac{B^2}{E^2}\right) \right],$$

(17)

to leading order in $1/N$. Of course, as $\Pi = TS$ in these systems, the average of the square of the Peltier coefficient is simply

$$\langle \Pi^2 \rangle = T^2 \langle S^2 \rangle.$$

(18)
Thus, the typical quantum dot will have a non-zero Seebeck and Peltier coefficients given by substituting Eq. (17) into Eqs. (1).

In the small temperature limit, this result coincides with that in the conclusions of Ref. [10]. To see this, one must note that $F(x, b) \propto x^2$ at small $x$, and take the fact that $E_{\text{Th}} \sim N \Delta$ for a dot level spacing of $\Delta$, as mentioned below Eq. (12b), so

$$\lim_{T \to 0} \langle S^2 \rangle \propto \frac{k_B^2}{e^2} \frac{k_B^2 T^2}{N^4 \Delta^2}$$

as in Refs. [10][33]. A careful reader will note that the numerical value of the constant of proportionality is a little different here from in Refs. [10,33], because of an ambiguity of order one in the choice of definition of $E_{\text{Th}}$, see our Eq. (12b).

However, the crucial point is that by finding the full $T$ dependence (see Fig. 2), we see that the quadratic growth with $T$ is only for extremely small $T$, and that $\langle S^2 \rangle$ has a maximum at $k_B T / E_{\text{Th}} \sim 0.5$ and $B \ll B_C$. Furthermore, the small $T$ the result goes like $N^{-4}$, rather than $N^{-2}$ when $k_B T$ is of order the Thouless energy, which is a huge difference for large $N$. This maximum value is

$$\langle S^2 \rangle_{\text{max}} \simeq 0.88 \times \left( \frac{1}{N} \frac{k_B}{e} \right)^2$$

It will be much smaller for $k_B T \ll E_{\text{Th}}$ or $k_B T \gg E_{\text{Th}}$. For large magnetic fields, $B \gg B_C$, the value of $\langle S^2 \rangle$ at any $T$ is half that with $B = 0$ at the same $T$.

The same quantity was also previously studied for small $N$; it was calculated analytically for $N_L = N_R = 1$ in Ref. [10] and numerically for $N_L = N_R = 2$ in Ref. [11], for a review see Ref. [12].

### 2.3 Average figure of merit

Substituting the averages in Section 2.1 into Eq. (8), we find that the average figure of merit is

$$\langle ZT \rangle = \frac{3}{\pi^2 N^2} \left[ F \left( \frac{k_B T}{E_{\text{Th}}}, 1 \right) + F \left( \frac{k_B T}{E_{\text{Th}}}, 1 + \frac{B^2}{B_C^2} \right) \right].$$

The non-monotonic behaviour of $\langle ZT \rangle$ with $T$ (shown by the curves for $F(x, b)$ in Fig. 2) can be understood intuitively by thinking of the dot’s discrete spectrum of randomly placed levels with a mean level spacing of $\Delta$. The coupling to the leads broadens these levels on the scale of $E_{\text{Th}} \sim N \Delta$. This means that for $N \gg 1$, the broadening is much greater than the spacing between levels, so the dot’s density of states is rather flat with small wiggles on the scale of $E_{\text{Th}}$. This implies the transmission as a function of energy is also rather flat, with small wiggles on the scale of $E_{\text{Th}}$. Temperature determines a window of energies, $k_B T$, on which transmission contributes to $ZT$. If this window is much less than $E_{\text{Th}}$, then the transmission is almost energy independent, and $ZT$ vanishes. If this window is much more than $E_{\text{Th}}$, then the transmission’s oscillations are on a much smaller scale than the window; They thus tend to cancel each other, which again means that $ZT$ vanishes. If this window is of order $E_{\text{Th}}$, then the transport is at its most sensitive to the fluctuations in transmission and $ZT$ is maximal. However, since the fluctuations in transmission are always small compared
to the average transmission, it is no surprise that \( \langle ZT \rangle \sim N^{-2} \ll 1 \) even at its peak. The conditions that maximize \( \langle ZT \rangle \) are the same as those that maximize \( \langle S^2 \rangle \) (from the curves in Fig. 2), we see this requires \( k_B T / E_{Th} \sim 0.5 \) and \( B \ll B_c \), and its maximum value is

\[
\langle ZT \rangle_{\text{max}} \simeq 0.27 \times \frac{1}{N^2}
\]

while it will be much smaller for \( k_B T \ll E_{Th} \) or \( k_B T \gg E_{Th} \). For large magnetic fields, \( B \gg B_c \), the value of \( \langle ZT \rangle \) at any \( T \) is half that with \( B = 0 \) at the same \( T \).

3 Universality of the Seebeck coefficient and figure of merit

Mesoscopic conductance fluctuations are well-known to have a “universal” magnitude, and are hence referred to as universal conductance fluctuations. This magnitude is given by the square-root of the variance

\[
\text{var}[G] = \left( \frac{e^2}{h} \frac{N_L}{N} \frac{N_R}{N} \right)^2 \times \text{(dimensionless function of } k_B T / E_{Th} \text{ & } B / B_c \text{)}
\]

where \( N = N_L + N_R \). Hence, they are “universal” in the sense that they do not change if one multiplies the width of all leads by the same amount (changing \( N \) without changing the ratios \( N_L/N \) or \( N_R/N \)). Actually, this is only true when \( \text{var}[G] \) does not depend on \( E_{Th} \) (i.e. at low enough temperature that \( k_B T \ll E_{Th} \)), because \( E_{Th} \) in Eq. (12) changes when one rescales the lead widths, whether or not one rescales the system size by the same amount as the lead widths.

Both the average figure of merit, \( \langle ZT \rangle \), and the typical magnitude of the Seebeck coefficient, \( \sqrt{\langle S^2 \rangle} \), depends on \( N \), and so are not “universal” in the same way as the universal conductance fluctuations. However, they are universal in the sense that they are independent of the ratios \( N_L/N \) or \( N_R/N \). For example, the value of \( \langle ZT \rangle \) or \( \langle S^2 \rangle \) is the same for a system with highly asymmetric leads with \( N_L = 100 \) and \( N_R = 300 \), as it is for a system with symmetric leads with \( N_L = N_R = 200 \). Unlike the universality of conductance fluctuations, this universality of \( \langle ZT \rangle \) and \( \langle S^2 \rangle \) holds for all \( T \), since \( E_{Th} \) in Eq. (12) depends on \( N \), but not on the ratios \( N_L/N \) or \( N_R/N \).

4 Full probability distributions

To calculate the full probability distribution of the thermoelectric coefficients, \( S \) and \( \Pi \), or the figure of merit, \( ZT \), we calculate all moments of these quantities. For large \( N \), we can use the same logic as above Eqs. (7) to write these moments as

\[
\langle S^{2m} \rangle = \frac{\langle I_4^{2m} \rangle}{\langle I_0 \rangle^{2m}} \left[ 1 + O[1/N] \right].
\]

\[
\langle (ZT)^m \rangle = \frac{\langle I_2^{2m} \rangle}{\langle I_0 \rangle^{m}} \left[ 1 + O[1/N] \right].
\]

for integer \( m \). It is also important to note that \( \langle S^{2m} \rangle \) goes like \( N^{-2} \), while \( \langle S^{2m+1} \rangle \) goes like \( N^{-3} \). Thus to leading order in \( 1/N \) we can take the odd moments of \( S \) to be zero. Of
Thus to calculate $\langle S^{2m} \rangle$ or $\langle (ZT)^{m} \rangle$, we need the average of $I_1^{2m}$ which contains the product of $2m$ transmission functions. This means that we need to calculate the average of arbitrary products of transmission functions. For this, it is convenient to use Eq. (10) to define $\delta T(E)$ as the fluctuations of the transmission away from its average value, $\langle T(E) \rangle$. As $\langle T(E_i) \rangle$ is independent of $E_i$, see Eq. (9), nothing changes if one replaces $T(E)$ by $\delta T(E_i)$ in the integrand of $I_1$. Thus

$$\langle I_1^{2m} \rangle = \int \frac{dE_1dE_2 \cdots dE_{2m}}{h^m} E_1f'(E_1) E_2f'(E_2) \cdots E_{2m}f'(E_{2m})$$

$$\times \langle \delta T(E_1)\delta T(E_2)\cdots \delta T(E_{2m}) \rangle, \quad (25)$$

where, without loss of generality, we have measured all energies from the electrochemical potential.

Then, the diagrammatics performed in section 5.3 gives us the averages of transmission functions in Eq. (25). For example, the average for $m = 4$ to leading order in $1/N$ is

$$\langle \delta T(E_1)\delta T(E_2)\delta T(E_3)\delta T(E_4) \rangle = \langle \delta T(E_1)\delta T(E_2) \rangle \langle \delta T(E_3)\delta T(E_4) \rangle$$

$$+ \langle \delta T(E_1)\delta T(E_3) \rangle \langle \delta T(E_2)\delta T(E_4) \rangle$$

$$+ \langle \delta T(E_1)\delta T(E_4) \rangle \langle \delta T(E_2)\delta T(E_3) \rangle, \quad (26)$$

where the three terms contain all possible pairwise combinations of $E_1, E_2, E_3, E_4$. Turning now to arbitrary $m$, the diagrammatic rules tell us that $\langle \delta T(E_1)\delta T(E_2)\cdots \delta T(E_{2m}) \rangle$ (to leading order in $1/N$) is a sum with $(2m)!/(2^m m!)$ terms, in which each term contains the product of pairwise averages, and the sum is over all pairwise combinations of $E_1, E_2, \cdots E_{2m}$ (with the ordering in each pair being irrelevant).

In the context of $\langle I_1^{2m} \rangle$ in Eq. (25), these sums over pairwise combination of energies are greatly simplified by the fact that we integrate over all energies. As a result each of the $(2m)!/(2^m m!)$ terms in the sum gives the same integral, each of which equals $m$ products of the integral in $\langle I_1^2 \rangle$. Thus

$$\langle I_1^{2m} \rangle = \frac{(2m)!}{2^m m!} \langle I_1^2 \rangle^m, \quad (27)$$

for any integer $m$. For what follows, we also note that the same rules easily give $\langle I_1^{2m-1} \rangle = 0$ for integer $m$ (to leading order in $1/N$). Substituting Eq (27) into Eq. (23) then gives

$$\langle S^{2m} \rangle = \frac{(2m)!}{2^m m!} \langle S^2 \rangle^m,$$

$$\langle S^{2m+1} \rangle = 0, \quad (28)$$

to leading order in $1/N$. Similarly, using Eq. (24), we see that the moments of the figure of merit are

$$\langle (ZT)^m \rangle = \frac{(2m)!}{2^m m!} \langle ZT \rangle^m, \quad (29)$$

to leading order in $1/N$.

Since these results give all moments of the probability distributions, one can find the probability distribution itself using the results in Appendix A. Then one sees that the probability distribution of $I_1$ is a Gaussian;

$$P(I_1) = \sqrt{\frac{1}{2\pi \langle I_1^2 \rangle}} \exp \left[-\frac{I_1^2}{2\langle I_1^2 \rangle}\right]. \quad (30)$$
4.1 Full distribution of the thermoelectric coefficients

Given Eqs. (4,30) we see that the Seebeck coefficient, $S$, has a Gaussian probability distribution,

$$P(S) = \sqrt{\frac{1}{2\pi\langle S^2 \rangle}} \exp\left[-\frac{S^2}{2\langle S^2 \rangle}\right].$$

(31)

This Gaussian at large $N$ was predicted from general arguments in Refs. [10, 11], without giving the form of $\langle S^2 \rangle$ outside the limit of small $T$. Our Eq. (17) gives $\langle S^2 \rangle$ for arbitrary $T$ and $B$, and hence completely determines the distribution of $S$ for large $N$. Turning to the Peltier coefficient, the fact that $\Pi = TS$ in these systems directly means that

$$P(\Pi) = (2\pi\langle \Pi^2 \rangle)^{-1/2} \exp\left[-\frac{\Pi^2}{2\langle \Pi^2 \rangle}\right].$$

One can compare the Gaussian distribution of $S$ at large $N$, with the distributions at small $N$ in Refs. [10] [11], they show discontinuities at small $S$ which are absent in the distribution at large $N$.

4.2 Full distribution of the figure of merit

Since $I_1$ follows a Gaussian distribution and $ZT$ goes like $I_1^2$, it is only take one line of algebra (see appendix A), to see that the distribution of $ZT$ is

$$P(ZT > 0) = \sqrt{\frac{1}{2\pi\langle ZT \rangle ZT}} \exp\left[-\frac{ZT^2}{2\langle ZT \rangle}\right].$$

while $P(ZT < 0) = 0$. This probability distribution is full determined by its average, $\langle ZT \rangle$, given in Eq. (21).

This distribution tells us that the probability a sample has a value of $ZT$ which is more than $\alpha$ times the average, is given by $1 - \text{erf}(\sqrt{\alpha}/2)$, where $\text{erf}(x)$ is an error function. It tells us that 2.5% of samples will have a value of $ZT$ which is more than 5 times bigger than the average, but only in 0.16% of samples will have a value of $ZT$ which is more than 10 times bigger than the average. The square-root divergence at small $ZT$ means there is a high probability of samples having smaller $ZT$ than average, for example there is a 25% chance that a sample has $ZT$ less than one tenth of the average.

5 Diagrammatics for open chaotic or disordered dots

This work uses the diagrammatic method developed in Refs. [13] [20] for correlations in transport, both quantum noise effects and conductance fluctuations, which built on the earlier work on mesoscopic corrections [21] [26]. These works showed that open quantum chaotic systems obey random matrix theory, as was already shown for closed systems in Refs. [27] [29], however in the process they developed simple diagrammatic rules to calculate averages of transmission functions which work for both random matrices and the semiclassical limit of quantum chaotic systems.

To draw the diagrams, one notes that the transmission function $T(E) = \sum_{ij} t_{ij}(E)t_{ij}^*(E)$, where $j$ is summed over all modes of the left lead, and $i$ is summed over all modes of the right lead. Here $t_{ij}(E)$ is the $ij$th element of the part of the system’s scattering matrix which
Figure 3: The leading order in $1/N$ contributions to $\langle \delta \mathcal{I}(E_1) \delta \mathcal{I}(E_2) \rangle$ without time-reversed trajectory-pairs; in other words, the trajectories in these contributions all go in the same direction in all trajectory pairs. These contributions are hence independent of the external $B$-field. The solid black trajectory correspond to a contribution to $t(E_1)$, and the dashed black trajectory corresponds to contribution to $t^*(E_1)$. The solid red trajectory correspond to a contribution to $t(E_2)$, and the dashed red one to contribution to $t^*(E_2)$. Note that contributions II and III are only different because of how they couple to the leads. Contribution II has the four paths together in an encounter at lead $L$, while they are in two pairs at lead $R$. In contrast, contribution III has the paths in two pairs at lead $l$, while the encounter is at lead $R$. One must have both these contributions.
corresponds to particles going from the left reservoir the the right reservoir. Each factor of \( t_{ij}(E) \) or \( t^*_ij(E) \) can be represented as a sum over all trajectories from left to right, so \( \mathcal{T}(E_1)\mathcal{T}(E_2) = \sum_{i_1j_1} \sum_{i_2j_2} t_{i_1j_1}(E_1) t^*_{i_2j_2}(E_2) t_{i_2j_2}(E_2) \), corresponds to four trajectories from left to right. It is convenient to draw the trajectories associated with factors of \( t(E) \) as solid lines and the trajectories associated with factors of \( t^*(E) \) as dashed line, and to use different colours for different energies. Any solid trajectory that is not paired with a dashed trajectory (and vice-versa) at every moment will average to zero. Broadly speaking, this is because each trajectory’s contribution to \( t_{ij}(E) \) is proportional to a factor whose phase is that trajectory’s action in units of \( \hbar \). If a trajectory is unpaired, its phase will be statistically independent of the phase of the other trajectories, and averaging over the ensemble will correspond to averaging over large fluctuations in the phase, which means the average will be zero. The simplest trajectory pairing is to pair the two trajectories with the same energy. This gives \( \langle \mathcal{T}(E_1)\mathcal{T}(E_2) \rangle = \langle \mathcal{T}(E_1) \rangle \langle \mathcal{T}(E_2) \rangle \). Given Eq. (10), such pairings give no contribution to \( \langle \delta\mathcal{T}(E_1)\delta\mathcal{T}(E_2) \rangle \), which means that the contributions to \( \langle \mathcal{T}(E_1)\mathcal{T}(E_2) \rangle \) come from more complicated pairings. Such more complicated pairings involve a solid trajectory paired with a given dashed trajectory for part of the time, but pairs meet at “encounters” where the pairings swap, for examples see Figs. 3 and 4. There are many such contributions, and only the ones at leading order in \( 1/N \) are discussed here.

The diagrammatic rules are derived in sections VI and VII of Ref. [17], and are summarized in Ref. [32] (although Ref. [32] also includes rules for superconducting reservoirs). The rules relevant here are as follows.

1. A trajectory-pair consisting of one solid trajectory with energy \( E_i \) and one dashed trajectory with energy \( E_j \) gives a factor of

\[
\frac{1}{N} \frac{1}{1 - i(E_i - E_j)/E_{Th} + \chi (B/B_c)^2},
\]

with \( \chi = 1 \) for time-reversed trajectories (marked with TR in Fig. 4) and with \( \chi = 0 \) otherwise.

2. A trajectory-pair that ends at lead \( i \) while not in an encounter, gives a factor of \( N_i \).

3. An encounter touching lead \( i \) gives a factor of \( N_i \), irrespective of how many trajectory-pairs meet at the encounter, and thereby end at the lead. This rule is not general, but applies to all the encounters touching leads that occur in the diagrams shown in this work.

4. An encounter inside the dot gives a factor \(-N \times (1 + \kappa)\). The factor of \((-N)\) is there for any encounter, no matter how many trajectories meet at the encounter. The \( N \)-independent factor of \( \kappa \) contains the encounter’s dependence on energy differences and B field, and depends on details of the encounter in the manner shown in Fig. 5. Note that \( \kappa = 0 \) for any encounter in the limit where all energies are equal (\( E_1 = E_2 \), etc) and there is no external magnetic field (\( B = 0 \)).

5.1 Diagrams for \( \langle T(E) \rangle \)

At leading order in \( 1/N \) there is only one diagram for \( \langle T(E) \rangle \), it is one in which the trajectories form a single pair from lead L to lead R. Thus there is one trajectory-pair and it is not time-reversed, thus its weight is given by rule 1 in the above list, with \( E_i = E_j = E \) and \( \chi = 0 \).
Figure 4: Leading order in 1/N contributions to $\langle \delta T(E_1)\delta T(E_2) \rangle$ which contain some time-reversed (TR) trajectory-pairs (some of the trajectory pairs consist of trajectories going in opposite directions). These time-reversed trajectory-pairs are marked with “TR”, such trajectory-pairs are cooperons in the language of disordered systems. Each diagram here corresponds on one in Fig. 3 but with the red trajectories passing though the encounters in the opposite way. However, this is not possible for the contributions in Fig. 3 with encounters at the leads (contributions II, III, and IV), meaning there are only the above three diagrams containing TR trajectory-pairs.

One end of the trajectory pair is on lead L and the other on lead R, with weights given by rule 2 in the above list. There are no encounters, so the other rules in the above list are not necessary. Thus we conclude that $\langle T(E) \rangle$ to leading order in 1/N is given by the result in Eq. (9).

5.2 Diagrams for $\langle \delta T(E_1)\delta T(E_2) \rangle$

To calculate the typical magnitude of the thermoelectric coefficients or the average figure of merit in the large N limit, we need to evaluate all the leading-order diagrams that contribute to $\langle \delta T(E_1)\delta T(E_2) \rangle$ to arrive at Eq. (11). These were discussed in Ref. [17, 18], and are shown in Fig. 3. Using the diagrammatic rules, one can convince oneself that these are the only diagrams that are order zero in N, and that all others (such as those including weak-localization loops) are higher order in 1/N. Thus, for large N, we only need to consider the diagrams in Figs. 3 and 4.

Giving weights to these diagrams following the above rules, we see that contribution I in Fig 3 has two encounters with $\kappa = 0$, so its total weight is

$$W_1 = \frac{N_L^2 N_R^2}{N^4} \left[ 1 + \frac{(E_2 - E_1)^2}{E_{Th}^2} \right]^{-1}. \quad (34)$$
The weights of contributions II, III and IV are

\[ W_{II} = -\frac{N_L N_R^2}{N^3} \left[ 1 + \frac{(E_2 - E_1)^2}{E_{Th}^2} \right]^{-1}, \tag{35} \]

\[ W_{III} = -\frac{N_L^2 N_R}{N^3} \left[ 1 + \frac{(E_2 - E_1)^2}{E_{Th}^2} \right]^{-1}, \tag{36} \]

\[ W_{IV} = \frac{N_L N_R}{N^2} \left[ 1 + \frac{(E_2 - E_1)^2}{E_{Th}^2} \right]^{-1}, \tag{37} \]

which means that they sum to zero; \( W_{II} + W_{III} + W_{IV} = 0 \).

Contributions V and VI have more complicated encounters with non-zero \( \kappa \). Contribution V has two encounters, with trajectories pairs contributing the same as in \( W_I \), however one encounter has \( \kappa = i(E_2 - E_1)/E_{Th} \) and the other has \( \kappa = -i(E_2 - E_1)/E_{Th} \), hence the contribution’s weight is

\[ W_V = \frac{N_L^2 N_R^2}{N^4}, \tag{38} \]

where the energy dependence that came from the encounters exactly cancelled the energy dependence that came from the trajectory-pairs. The contribution VI has an encounter with \( \kappa = i(E_2 - E_1)/E_{Th} \), hence the contribution’s weight is

\[ W_{VI} = -\frac{N_L^2 N_R^2}{N^4}, \tag{39} \]

where again there is exact cancellation between the energy dependence that came from the encounter and that which came from the trajectory-pair. Hence, these two contributions also sum to zero; \( W_V + W_{VI} = 0 \).

Now we turn to the contributions which involve some time-reversed trajectory-pairs, which are shown in Fig. [4]. The contribution I-TR has encounters with the same weight as contribution I, but with the trajectory-pairs marked with “TR” have extra factors of \( (B/B_c)^2 \) in the denominator, hence its weight is

\[ W_{I-TR} = \frac{N_L^2 N_R^2}{N^4} \left[ 1 + \frac{(E_2 - E_1)^2}{E_{Th}^2} + \frac{B^2}{B_c^2} \right]^{-1} \tag{40} \]

The contributions V-TR and VI-TR are similar to those of V and VI, but both the encounters and the trajectory pairs have extra factors of \( (B/B_c)^2 \). Remarkably, these factors are arranged in such a manner that they all cancel, and the contributions are \( B \)-independent. Thus

\[ W_{V-TR} = -W_{IV-TR} = \frac{N_L^2 N_R^2}{N^4} \tag{41} \]

so again these two contributions sum to zero. Note that it would be very odd if contributions V-TR and VI-TR did not sum to zero, since one expects on general grounds that the correlations decay with increasing \( B \), so non-cancelling \( B \)-independent contributions should not exist.

Thus, in conclusion, the sum of all contributions to \( \langle \delta \mathcal{F}(E_1) \delta \mathcal{F}(E_2) \rangle \) is equal to the sum of the weights of contributions I and I-TR, and this is what is given in Eq. (11).
Value of $\kappa$: $-i \frac{E_2 + E_3 - E_1 - E_4}{E_{Th}}$

Value of $\kappa$: $-i \frac{E_2 + E_3 - E_1 - E_4 + B^2}{E_{Th} B_c^2}$

Value of $\kappa$: $-i \frac{E_2 + E_4 + E_5 - E_1 - E_3 - E_6}{E_{Th}}$

Value of $\kappa$: $-i \frac{E_2 + E_4 + E_5 - E_1 - E_3 - E_6 + B^2}{E_{Th} B_c^2}$

Figure 5: An encounter’s contribution is $-N \times [1 + \kappa]$, where $\kappa$’s dependence on energies and the magnetic field is different for different encounters. The value of $\kappa$ for various encounters is given here. Sections VI and VII of Ref. [17] explain the origin of these contributions.
5.3 Diagrams for higher order correlators

The objective of this section is to argue that the diagrammatic rules tell us that an $M$th order transmission correlators of the form $\langle \delta T(E_1) \delta T(E_2) \cdots \delta T(E_M) \rangle$, is given by all possible pairwise groupings of the transmission coefficients, see in and below Eq. (26).

The $M$th order transmission correlators of the form $\langle \delta T(E_1) \delta T(E_2) \cdots \delta T(E_M) \rangle$, consists of $2M$ trajectories from lead L to lead R, as sketched on the left in Fig. 6. Such contributions average to zero unless all the trajectories they contain are paired up at all time (switching pairing at encounters). In addition, because of the definition in Eq. (10), a contribution is also zero if any trajectory is only paired with its partner of the same energy.

We will see that for large $N$, the leading order contributions to this correlation are of order $N^0$, with corrections going like $1/N$. With this in mind, our objective is to find all ways of pairing the $2M$ trajectories in manners that give a contribution at order $N^0$.

We start by taking the first pair of trajectories (those with energy $E_1$) and connecting them with the $i$th pair of trajectories (those with energy $E_i$), such that they meet at encounters and exchange pairings. This connection can be via any of the diagrams in Figs. 3, 4, all of which are order $N^0$. If we now take the $j$th pair of trajectories (those with energy $E_J$, and try to connect them (via encounters) with trajectories of pair 1 or pair $i$, we find we always get a diagram which is of order $1/N$ or smaller. Thus to get a contribution of order $N^0$, we must connect the $j$th pair with another pair which has not yet been involved in any encounters (i.e. the pair with energy $E_k$ for $k \neq 1, i, j$). Trajectories that are not connected are statistically independent, and so can be averaged separately. Thus order $N^0$ contributions are those where each trajectory pair with exactly one other, all other contributions are smaller, and so can be neglected. The result is that for $M = 4$, we get Eq. (26), and for even $M$ (so $M = 2m$ with integer $m$) we get the result outlined below Eq. (26). In contrast for odd $M$, there is an odd number of trajectory pairs, and so one cannot connect each pair with one other (there will always be a pair left over). Thus $\langle \delta T(E_1) \delta T(E_2) \cdots \delta T(E_M) \rangle$ is of order $1/N$ for odd $M$, which means we can take it to be zero when working at order $N^0$.

6 Conclusions

Here, we provide a quantitative theory for the thermoelectric response and the figure of merit of large open quantum dots. The dots may be disordered or chaotic, and are coupled to two leads, left (L) and right (R), which carry a large number of modes, $N \gg 1$. Such systems have long been know to have a rather weak thermoelectric response, however to the best of our knowledge no quantitative results existed outside the regime of very low temperatures. Quantitative theories such as this are necessary, if one wishes to use the thermoelectric response as a probe of a the physics of nanostructures.

We show that the thermoelectric response of such systems is always small, but is peaked when the temperature is half the Thouless energy, and when the external magnetic flux through the dot is zero. This condition maximises both the typical Seebeck and Peltier coefficients, $S_{\text{typical}}$ and $\Pi_{\text{typical}}$, and the average thermoelectric figure of merit, $\langle ZT \rangle$. These quantities are also found to exhibits a type of universality, in the sense that it does not depend on the asymmetry between the number of modes in lead L and R, but only on the sum of the two, $N = N_L + N_R$. 

17
Figure 6: Contributions to $\langle \delta T(E_1)\delta T(E_2)\cdots\delta T(E_M) \rangle$ for $M = 7$. On the left, each $\delta T(E_i)$ is represented by two trajectories of the same colour joined at beginning and end. Only contributions where the trajectories are connected contribute to the average. On the right, we show one possible way of connecting them. All trajectories are in pairs, but they swap pairings at the encounters (black rectangles). If any colour is paired with itself alone, then its contribution is zero. The full contribution is the product of the individual connected contributions. The connected contributions involving only two pairs of trajectories (such as black-green or red-blue here) are zeroth order in $1/N$, Those involving three or more pairs of trajectories are higher order in $1/N$; for example the connected contribution involving three colours (orange-purple-cyan) is of order $1/N$. Thus the product over all connected contributions will be of order $N^0$, if all connected contributions involve only two pairs of trajectories (i.e. two colours). See section 5.3 for more details.
A From moments to probability distribution

In section 4, we have a probability distribution, \( P(y) \), whose moments obey

\[
\langle y^{2m-1} \rangle = 0, \quad \text{and} \quad \langle y^{2m} \rangle = \frac{(2m)!}{2^m m!} \langle y^2 \rangle^m, \tag{42}
\]

for integer \( m \), where \( \langle \cdots \rangle = \int dy P(y) (\cdots) \). For a Gaussian probability distribution,

\[
P(y) = \sqrt{\frac{\alpha}{\pi}} \exp \left[-\alpha y^2\right], \tag{43}
\]

with \( \alpha = 1/(2\langle y^2 \rangle) \), one can calculate the moments, and see that they obey Eq. (42).

If one wishes to prove this in a deductive manner, rather than via the above observation, one can start by defining the generating function

\[
F(t) \equiv \langle e^{iyt} \rangle = \sum_{n=0}^{\infty} \frac{it^n \langle y^n \rangle}{n!}. \tag{44}
\]

This means that \( F(t) = \int dy e^{iyt} P(y) \), and hence the probability distribution, \( P(y) \), can be found from \( F(t) \) via the Fourier transform,

\[
P(y) = \int \frac{dt}{2\pi} e^{-iyt} F(t). \tag{45}
\]

Thus, once one has \( F(t) \), one can find \( P(y) \).

In the case of interest here, substituting Eq. (42) into Eq. (44), we define \( n = 2m \), and find that

\[
F(t) = \sum_{m=0}^{\infty} \frac{(-t^2 \langle y^2 \rangle)^m}{2^m m!} = \exp \left[-\frac{1}{2} \langle y^2 \rangle t^2\right]. \tag{46}
\]

Thus, the Fourier transform gives

\[
P(y) = \sqrt{\frac{1}{2\pi \langle y^2 \rangle}} \exp \left[-\frac{y^2}{2\langle y^2 \rangle}\right]. \tag{47}
\]

Next we wish to consider the probability distribution \( P(z) \), whose moments obey

\[
\langle z^m \rangle = \frac{(2m)!}{2^m m!} \langle z \rangle^m, \tag{48}
\]

By comparison with Eq. (42), we see that it is the same with \( z = y^2 \), and we can use this fact to get \( P(z) \) from Eq. (47). We have \( P(z) dz = 2P(y) dy \), where the factor of two is due to contributions to \( P(z) \) from both positive and negative \( y \), hence

\[
P(z) = 2P(y)|_{y=\sqrt{z}} \frac{d}{dz} \sqrt{z} = \sqrt{\frac{1}{2\pi \langle z \rangle z}} \exp \left[-\frac{z}{2\langle z \rangle}\right], \tag{49}
\]

which is an exponential decay with square-root divergence at small \( z \).
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[43] This is what leads to the well known results that for any realisation of the chaos or disorder, the electrical conductance $G = \langle G \rangle [1 + O(1/N)]$, while the thermal conductance $K = \langle K \rangle [1 + O(1/N)]$. 