Anomalous electronic shot noise in resonant tunneling junctions

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(Dated: February 19, 2019)

Abstract: We study the behavior of shot noise in resonant tunneling junctions far from equilibrium. Quantum-coherent elastic charge transport can be characterized by a transmission function, that is the probability for an incoming electron at a given energy to tunnel through a potential barrier. In systems such as quantum point contacts, electronic shot noise is oftentimes calculated based on a constant (energy independent) transmission probability, a good approximation at low temperatures and under a small bias voltage. Here, we generalize these investigations to far from equilibrium settings by evaluating the contributions of electronic resonances to the electronic current noise. Our study extends canonical expressions for the voltage-activated shot noise and the recently discovered delta-T noise to the far from equilibrium regime, when a high bias voltage or a temperature difference is applied. In particular, when the Fermi energy is located on the shoulder of a broad resonance, we arrive at a formula for the shot noise revealing anomalous-nonlinear behavior at high bias voltage.

I. INTRODUCTION

Noise in electronic signals is typically undesired, yet it can be a source of information on the conducting system, by exposing effects concealed in the time-averaged electric current [1, 2]. Shot noise measurements at the mesoscale and nanoscale reveal the fractional charge of quasiparticles in many-body systems [3]. Contributions of different channels to the transport [4, 5], the crossover from ballistic to diffusive mechanism [6], the valence orbital structure of the contact [7, 8], activation of vibrations in molecular conducting junctions [9–11], and the onset of spin-polarized transport [12] are among overlooked, anomalous shot noise terms, which are proportional to the temperature and the linear response electronic conductivity. When a voltage bias is applied across the conductor, voltage-induced shot noise is activated, and it dominates over the thermal noise at high bias and low temperatures. Furthermore, temperature differences across channels activate an additional white-noise contribution, the recently measured ‘delta-T’ noise, which is quadratic in the temperature difference [20].

Recent measurements of shot noise in quantum point contacts of gold revealed a nonlinear (termed ‘anomalous’) noise-voltage behavior at high bias and low temperatures [21]. These observations, as well as other measurements at elevated temperatures [22, 23] are anomalous in the sense that they do not follow the standard theoretical prediction [see Eqs. (1) and (2) below]. We recall that to derive the standard formulae, the transmission probability of electrons to cross the constriction is assumed to be a constant, evaluated at the equilibrium Fermi energy [2].

Different mechanisms were suggested to explain observations of anomalous shot noise. For example, it may arise due to local heating of electrons [22], interference effects due to scatterings with impurities located at the electrodes at the vicinity of the point contact [21], electron-electron and electron-phonon inelastic effects [22, 23]. Correspondingly, recent theoretical works focused on the behavior of shot noise while taking into account electron [24–26], and spin [27] correlations, as well as electron-phonon inelastic effects [28–30]. Approximately, the impact of such processes can be captured within the elastic transport theory by using a voltage, and/or temperature dependent transmission function [21, 22]. Nevertheless, a consistent explanation to the variety of experimental observations of anomalous shot noise is still missing, even for the well-studied metallic (gold) break junction setup [21, 22].

The objective of our work is to revisit the (seemingly solved) problem of electronic shot noise in quantum coherent nanostructures, and study the behavior of shot noise in far from equilibrium situations, that is at high bias voltage or under large temperature differences. Recent studies have put forward complex mechanisms for explaining observations of anomalous shot noise, e.g. relying on many body effects. In contrast, here we carefully examine the analytically tractable problem of elastic conduction in resonant tunneling junctions and bring to light an overlooked, anomalous shot noise term, which is building up far from equilibrium. We emphasize that we restrict our analysis to the flat noise spectrum component.

When electron transport is quantum coherent, quantum chemistry computations can be readily performed to take into account the rich electronic structure of the
FIG. 1. Schematic representation of the different analytical results for the current noise as a function of voltage. Under the assumption of a constant transmission, the current noise obeys Eq. (4), illustrated here at high (full) and low (dashed) temperatures. Taking into account the variation of the transmission function with energy we arrive at Eq. (11), simulated here at low temperature (dotted). Panels (a)-(c) depict tunnel junctions with a single impurity level bridging two metal electrodes (a) at thermal equilibrium, (b) under low bias voltage at zero temperature, and (c) under high bias voltage at zero temperature. The Lorentzian lineshape illustrates the broadening of the level (resonance). Horizontal dashed lines mark the bias window relevant for charge transport. The behavior of the noise in the three different cases is marked on the noise-voltage curve.

conducting channel (atoms or molecules), as was recently done in Ref. [32]. However, our goal here is to provide a more general understanding of shot noise based on analytic calculations. Specifically, we aim to to derive formulae for the nonequilibrium zero frequency noise, which would be useful for experimentalists in their efforts to pinpoint the origins of observed anomalous noise.

We consider resonant tunneling junctions under bias voltage or a temperature difference and focus on the role of the transmission resonance on transport. Our central achievements are: (i) Under bias voltage, we derive a closed-form expression for the shot noise—valid for broad resonances—exposing the nonlinearity of the shot noise with bias at low temperature. In Fig. 1 we sketch the behavior of shot noise in quantum coherent conductors under low or high bias voltage, illustrating our results. (ii) For junctions under a temperature difference, we show that the $(\Delta T)^2$ scaling of the shot noise, as observed in Ref. [21] is robust and it survives even when the the transmission function depends on energy.

The paper is organized as follows. In Sec. II we review the standard (‘normal’) shot noise expressions for the current noise, received under the assumption of a constant transmission probability. In Sec. III we go beyond this assumption and present analytic results for the current noise; details are left to Appendices A-E. We exemplify our derivations with simulations in Sec. IV and conclude in Sec. V.

II. STANDARD RESULTS: CONSTANT TRANSMISSION PROBABILITY

We consider coherent, elastic transport of electrons in a two-terminal junction. The metals $L$ and $R$ include collections of noninteracting electrons with occupation numbers following the grand canonical ensemble; the Fermi function $f(\epsilon, \mu_\nu, T_\nu) = \frac{1}{e^{\beta_\nu(\epsilon - \mu_\nu)} + 1}$ is evaluated at the chemical potential $\mu_\nu$ and temperature $T_\nu$ with the inverse temperature $\beta_\nu = 1/k_B T_\nu$; $\nu = L, R$. Below we denote by $\mu$ the equilibrium Fermi energy. Ignoring decoherence and inelastic processes within the constriction, the average current is given by the Landauer formula with the transmission $\tau(\epsilon)$,

$$\langle I \rangle = \frac{2e}{h} \int_{-\infty}^{\infty} d\epsilon \tau(\epsilon) [f(\epsilon, \mu_L, T_L) - f(\epsilon, \mu_R, T_R)]. \tag{2}$$

The corresponding zero frequency power spectrum of the noise is given by...
For simplicity, we omit the reference to (zero) frequency. In this partition of the total noise, $S_1$ includes additive terms in the left and right metals while $S_2$ collects transport processes from one terminal to the other. The transmission function portrays the conducting wire, thus the transmission function $\tau(\epsilon)$ is energy dependent; voltage and temperature dependency, rooted in many-body effects, are sometimes phenomenologically introduced into the transmission function—though not in our work.

Let us now review the standard, ‘normal’ shot noise expressions, which are used to fit experimental observations. Equations (2)-(3) can be simplified if $\tau(\epsilon)$ is assumed a constant. This assumption is justified at low bias and under a small temperature difference. Then, the width of resonances (responsible for charge transport through the system) is considerable relative to the bias window, thus the transmission function can be approximated by its (fixed) value at the Fermi energy, see Fig. 1b). Making this critical assumption, the averaged current under a finite voltage reduces to $\langle I \rangle = \frac{2e}{h} \Delta \mu \sum_i \tau_i$, with the power noise $S_{\Delta \mu} = 4k_B T G_0 \sum_i \tau_i^2$

$$S_{\Delta \mu} = 4k_B T G_0 \sum_i \tau_i^2 + 2\Delta \mu \coth \left( \frac{\Delta \mu}{2k_BT} \right) G_0 \sum_i \tau_i (1 - \tau_i).$$

Here, $T = T_{L,R}$ and $\Delta \mu = \mu_L - \mu_R = eV$ is the chemical potential difference due to the bias voltage $V$, $G_0 = 2e^2/h$ is the quantum of conductance. The current and the power noise include contributions from several channels, with $\tau_i$ the transmission probability of the $i$th channel evaluated at the equilibrium Fermi energy $\mu = (\mu_L + \mu_R)/2$ of the metal leads; the chemical potential is shifted symmetrically between the $L$ and $R$ terminals. Eq. 4 is well known; we retrieve it in Appendices A-B as a special limit of a more general expression.

Noise measurements in atomic-scale and molecular junctions performed at low bias well agree with Eq. 4, see for example Refs. [2-5]. Specifically, when the temperature is low relative to the bias, $\coth(\Delta \mu/(2k_BT)) \to 1$, and we get

$$S_{\Delta \mu \to 0} = 2|\Delta \mu| GF.$$

Here, $F = \sum_i \tau_i (1 - \tau_i)/\sum_i \tau_i$ is the Fano factor, $G = G_0 \sum_i \tau_i$ stands for the electrical conductance and $e$ is the charge of the electron. Equation 5 is linear in voltage; nonlinearity of the low-temperature high-bias shot noise with voltage is referred to as an ‘anomalous’ behavior. Since $\langle I \rangle = GV$ and $\Delta \mu = eV$, we can organize Eq. 5 in its familiar form as $S_{\Delta \mu \to 0} = 2e\langle I \rangle |F|$, which vanishes, and that the power noise Eq. 3 simplifies to

$$S_{\Delta \mu \to 0} = 4k_B T G_0 \sum_i \tau_i + \left[ \frac{k_B (\Delta T)^2}{T} \left( \frac{2\pi^2}{3} - \frac{2}{3} \right) \right] G_0 \sum_i \tau_i (1 - \tau_i).$$

Here, $\bar{T} = (T_L + T_R)/2$ is the averaged temperature. This result was derived in Ref. 20, see also Appendix C. The excess (nonequilibrium) delta-T noise, which is the second term in Eq. 4 displays three particular characteristics: (i) It is quadratic in the temperature difference, (ii) it is inversely proportional to the average temperature, and (iii) as a partition noise, it is proportional to the factor $\sum_i \tau_i (1 - \tau_i)$.

In what follows, we ask the following question: How do we generalize Eqs. 4 and 5 to junctions with an energy dependent transmission function, termed here ‘resonant tunneling junctions’? The variation of the transmission function with energy should be taken into account in atomic and molecular junctions when the voltage bias or the temperature differences are large such that contributions of carriers beyond the Fermi energy become substantial, see Fig. 1.

III. ANOMALOUS NOISE FAR FROM EQUILIBRIUM

The transmission function portrays the conducting junction: it is peaked at energies of charge conducting atomic/molecular orbitals (resonances) and its width reflects the hybridization energy of that state to the metal.
electrodes. The approximation of a constant transmission probability is meaningful only close enough to equilibrium, when the width of the transmission function (dictated by the coupling energy of the atomic chain or molecule to the electrodes) is broad relative to the bias window. Without committing to a particular form, we write down a Taylor expansion for the transmission function, performed around the equilibrium Fermi energy $\mu$,

$$\tau(\epsilon) \approx \tau(\mu) + \left. \frac{d\tau}{d\epsilon} \right|_{\mu} (\epsilon - \mu). \quad (8)$$

For simplicity, we denote $\tau(\mu)$ by $\tau_0$ and $\tau'(\mu) \equiv \left. \frac{d\tau}{d\mu} \right|_{\mu}$. As a specific example, consider a resonant level with a single orbital at energy $\epsilon_d$ and broadening $\Gamma_{L,R}$ from the left and right metals. The transmission function is given by

$$\tau(\epsilon) = \frac{\Gamma_L \Gamma_R}{(\epsilon - \epsilon_d)^2 + (\Gamma_L + \Gamma_R)^2/4}. \quad (9)$$

Assuming a broad resonance shifted from the Fermi energy, the Lorentzian can be approximated by Eq. (8) with

$$\tau_0 = \frac{\Gamma_L \Gamma_R}{(\epsilon_d - \mu)^2 + (\Gamma_L + \Gamma_R)^2/4}, \quad \tau'(\mu) = \frac{2(\epsilon_d - \mu)\Gamma_L \Gamma_R}{[\mu - \epsilon_d]^2 + (\Gamma_L + \Gamma_R)^2/4}. \quad (10)$$

Our analytical work does not assume the Lorentzian line-shape for the transmission function; numerical simulations reported in Sec. IV adopt this form.

We now present the main results of our work. We substitute Eq. (8) into Eq. (3), evaluate integrals, and simplify the result in different limits. For simplicity, we consider only a single transport channel.

### A. Voltage-activated noise

We derive a closed-form expression for the voltage-activated noise at nonzero temperature $T$. Details are given in Appendix B. Our expression can be organized in various ways to highlight its different properties. Here, we write it down in a manner that features its dependence on the scaled voltage, defined as

$$4k_B T G_0 \left[ \frac{\Delta \mu}{2k_B T} \coth \left( \frac{\Delta \mu}{2k_B T} \right) - 1 \right] \tau_0 (1 - \tau_0) \quad (11)$$

as we depart from equilibrium by applied voltage.

Overall, based on Eq. (11) we conclude that: (i) Excess current noise is a concave function of the scaled voltage, in agreement with experimental observations [21, 22]. However, (ii) Eq. (11) predicts the suppression of the excess noise at high voltage relative to the constant $\tau$ expression, rather than an enhancement, as observed in e.g. Ref. [22]. Nevertheless, we point out that when other factors are at play (essentially, many-body interactions and the opening of additional channels at high voltage), the transmission function can effectively increase with voltage. Combining this effect with the concave functional form would result in an overall enhancement of the noise—on top of a downward curved function.

Experimentally, one could assess this expression by first studying the behavior of the noise at low bias as a
function of the scaled voltage, to extract the linear trend and the associated $\tau_0$ value. Then, subtracting this contribution from the noise at high bias one could test the applicability of the nonlinear terms [last two lines in Eq. (11)] to the specific case.

Equation (11) allows us to quickly retrieve the equilibrium noise, given by

$$S_{\Delta \mu = 0}^T = 4k_B T G_0 \tau_0,$$

which is identical to the case of a constant transmission function. This is expected since Eq. (6) is correct in general for an arbitrary $\tau(\epsilon)$.

We now examine the low temperature limit of Eq. (11), $\Delta \mu \gg 2k_B T$. We obtain the following anomalous, nonlinear shot noise,

$$S_{\Delta \mu \to 0}^T = 2G_0 \tau_0 (1 - \tau_0)|\Delta \mu| - G_0 [\tau'(\mu)]^2 \frac{|(\Delta \mu)|^3}{6}$$

This expression is one of the central results of our work. It exposes a cubic dependence of the power noise on bias voltage, on top of the regular linear behavior [compare Eq. (13) to Eq. (5)]. It assumes low temperature, $k_B T \ll \Delta \mu$, but under this assumption the result is exact for arbitrarily large bias—to the $\tau'(\mu)$ order considered.

We can also Taylor-expand Eq. (11) in bias voltage at nonzero temperature. We observe a quadratic noise-voltage behavior even when taking into account the structure of the transmission function,

$$S_{\Delta \mu \ll T}^T = 4k_B T \tau_0 G_0 + 2G_0 \tau_0 (1 - \tau_0) \frac{\Delta \mu^2}{6k_B T}$$

$$\quad - 2G_0 [\tau'(\mu)]^2 \frac{\Delta \mu^2}{3} k_B T \left( \frac{\pi^2}{6} - 1 \right).$$

Unlike Eq. (13), this formula is only valid close to equilibrium.

Overall, our results in this section demonstrate that including the resonance structure leads to noise suppression. In Figs. 2-4 we assess the accuracy of Eq. (11), as well as the impact of sharp resonances on the noise.

### B. Delta-T noise

Delta-T noise is activated by temperature differences as implied by its name; measurements display a quadratic behavior of the noise with the temperature difference $2^4$. Indeed, the theoretical analysis of Ref. $2^0$ confirmed this trend for a constant transmission function, see Eq. (4). However, far from equilibrium, that is at large temperature differences, the structure of the transmission function (resonance) should be taken into account in the noise calculation, which is what we set to do here.

Substituting Eq. (8) into Eq. (5) we collect quadratic $(\Delta T)^2$, and quartic $(\Delta T)^4$ contributions to the delta-T noise, see Appendices C and D. We find that quartic terms are order of magnitude smaller than the quadratic delta-T noise—even in the most extreme nonequilibrium case of $\Delta T = 2T$. The full expression to the quartic order is quite cumbersome, and here we write it down as

$$S_{\Delta T} = 4k_B T \tau_0 G_0 + G_0 k_B \tau_0 (1 - \tau_0) \left[ a_1 \frac{(\Delta T)^2}{T^2} - a_2 \frac{(\Delta T)^4}{T^4} \right]$$

$$\quad - G_0 [\tau'(\mu)]^2 k_B^3 T^3 \left[ b_1 \frac{(\Delta T)^2}{T^2} - b_2 \frac{(\Delta T)^4}{T^4} \right].$$

The coefficients $a_{1,2}$ and $b_{1,2}$ are given in Appendix D, and they satisfy $a_2/a_1 \sim 1/40$ and $b_2/b_1 \sim 0.1$. Therefore, for the delta-T noise there is no analog to the anomalous term $[\tau'(\mu)]^2 |(\Delta \mu)|^3$ of equation (13). Here, in contrast, the quadratic order persists even far from equilibrium when the transmission resonance is taken into account. Disregarding the quartic terms we get (see Appendix D),

$$S_{\Delta T} = 4k_B T \tau_0 G_0 + G_0 k_B \tau_0 (1 - \tau_0) \left( \frac{\pi^2}{9} - \frac{2}{3} \right)$$

$$\quad - G_0 [\tau'(\mu)]^2 \left( \frac{7\pi^4}{45} - 4 \frac{\pi^2}{3} \right) k_B^3 T (\Delta T)^2. \quad (16)$$

Equation (15), the ‘delta-T resonant tunneling noise’ generalizes Eq. (4). It displays three central characteristics: (i) It is quadratic in $\Delta T$. (ii) The third (new) contribution reduces the noise, compared to the case with a constant transmission. (iii) The third term grows with the average temperature, unlike the second term. (iv) As mentioned above, the quadratic $(\Delta T)^2$ dependence is robust; the contribution of the quartic term in the delta-T noise is very small, even when taking into account the energy dependence of the transmission function. This result is demonstrated in Fig. 5 which is discussed in the next section.

### IV. SIMULATIONS

We use simulations to assess the validity of our analytic expressions from Sec. IIII Assuming coherent tunneling through a single level as described by Eq. (9), the authors of Ref. $2^5$ demonstrated a rich behavior of the voltage-activated current noise as a function of gate voltage. Here, we present simulations with three objectives in mind. First, assuming the Fermi energy is placed on the shoulder of a broad resonance we exemplify the usefulness of the analytic results of Sec. IIII and relate simulations to experimental observations. Second, we perform simulations for narrow resonances, which are not captured by our theory. Here, we illustrate a significant nonlinearity of the power noise with voltage far from equilibrium (at low temperature), reproducing some of the observations reported in Ref. [21]. Lastly, we demonstrate that while the voltage-activated resonant tunneling noise displays ‘anomalous’ characteristics for narrow resonances at high voltage, the delta-T resonant tunneling noise shows a robust quadratic behavior even far from equilibrium.
In simulations we adopt a Lorentzian function, Eq. (9), and assume spatial symmetry, $\Gamma = \Gamma_{L,R}$. Numerical results based on Eq. (3) are compared to the ‘normal’ constant transmission expressions of Sec. II and to the ‘resonant tunneling’ results of Sec. III.

![Image](image1.png)

**FIG. 2.** Current and current noise in a tunnel junction with a broad resonance. (a) Lorentzian transmission function located at $\epsilon_d = 0.4$ eV with $\Gamma = 0.5$ eV. We further present the Fermi function window at $\Delta \mu = 0.5$ and mark the transmission value at the Fermi energy, $\tau_0 = 0.61$. (b) Current-voltage characteristics using the transmission function from panel a. (c) Excess current noise as a function of voltage: (full) Numerical calculations with a Lorentzian function using Eq. (3). (dashed) Constant transmission expression, Eq. (4) with $\tau_0 = 0.61$. (dashed-dotted) Resonant-tunneling result, Eq. (11). The light dotted line identifies the bias $\Delta \mu = 0.5$ eV, corresponding to the bias window in panel (a). Simulations were performed at $T = 10$ K.

### A. Voltage-activated noise

Roughly, given the low-order Taylor expansion in Eq. (8), Eq. (11) is valid as long as $|\tau'(\mu)/(\Delta \mu)|$ is smaller than $\tau_0$, which is the case when the Fermi energy is placed on the shoulder of a broad resonance, $|\Delta \mu| < 2|\epsilon_d - \mu|$ and $\Gamma_{L,R} > \Delta \mu$.

In Fig. 3 we present the current and the excess noise at low temperature using a broad transmission function centered at $\epsilon_d = 0.4$ eV; the Fermi energy is set at zero. We expect Eq. (11) to hold as long as $\Delta \mu < 0.8$, i.e. before the bias window covers the peak of the resonance. The current-voltage characteristics displayed in panel (b) is quite linear in the full range, which is expected when using the expansion $\tau(\epsilon) = \tau_0 + \tau'/(\epsilon - \mu)$, $I = \tau_0 G_0 \Delta \mu$. The current noise is linear in bias close to equilibrium; note that the temperature is quite low. However, at high bias the current noise as computed numerically from Eq. (3) clearly deviates from the linear trend predicted by Eq. (5). In contrast, the resonant tunneling formula, Eq. (11), provides an excellent match up to $\Delta \mu = 0.65$ eV. This agreement is substantial given that at this point the bias window covers a large portion of the transmission function, see Fig. 2(a). Simulations were performed at 10 K, but similar results were observed for $T=0.1$-300 K.

As mentioned above, Eqs. (11)-13 should be used with care: They are invalid once the voltage window ex-
tends over the peak of the resonance. Specifically, close to the extremum ($\tau(\mu) = 1$ here), the low order, linear expansion \[5\] is obviously insufficient. Thus, when $\tau_0$ is large, our analytic results hold only at low bias voltage. This point is illustrated in Fig. \[3\] with $\epsilon_d$ placed close to the Fermi energy, at $\epsilon_d = 0.2$ eV. We observe in panel (c) that Eq. \[13\] is credible only for $\Delta \mu < 0.35$ eV. Beyond that, Eq. \[11\] critically fails and in fact (incidently) the constant transmission approximation provides a more accurate result.

It is clear that our results, which are based on a low-order expansion \[5\], do not hold if the resonance is narrow compared to the bias voltage. In Fig. \[3\] we study this situation, resorting to direct numerical evaluation of Eq. \[4\]. As we show in panel (c), the excess current noise increases linearly at low bias, and it displays a kink around $\Delta \mu = 0.2$ eV followed by a further increase of noise. Overall, the noise is concave in voltage and it is nonlinear, or ‘anomalous’. At the same time, the differential conductance is symmetric in voltage, see panel (b). These concurrent characteristics for the conductance and the noise were reported in Ref. \[21\]. Our results quantitatively reproduce these measurements; by further modifying $\epsilon_d$ and $\Gamma$ a precise agreement with Ref. \[21\] can be reached.

It should be pointed out that along with measurements that are reproduced here in Fig. \[4\] other junctions examined in Ref. \[21\] displayed more compound, anomalous trends, which are not predicted by our expressions. These results were explained in Ref. \[21\] based on interference effects with impurities at the metal electrodes. By further complicating our theory to e.g. emulate many-body interactions, achieved by turning $\tau(\epsilon)$ into a function of voltage and temperature, it should be possible to reproduce more complex noise trends. We emphasize however that our objective here has been to stay with the simple and rigorous coherent transport model and analytically resolve nonlinear characteristics.

\section*{B. Delta-T noise}

We study the Delta-T noise, that is shot noise generated by $\Delta T$ in Fig. \[5\]. As explained in Sec. \[11\] the quadratic formula is robust—as long as the expansion \[5\] is valid. Fig. \[5\] confirms that (i) Eq. \[10\] provides a very good approximation to the exact (numerically computed) noise. (ii) Far from equilibrium, the constant transmission formula Eq. \[7\] overestimates the excess noise, yet it properly predicts the quadratic behavior. We further present in panel (d) the excess noise at lower temperature, $T = 30$ K, which corresponds to experimental studies \[21\]. In this case we confirm that the constant transmission expression \[7\] is highly accurate.

It is useful to note that under the strict assumption of a constant transmission, the electric current vanishes; charge current showing up in panel (c) emerges from the contribution of $\tau(\mu)$,

\[
\langle I \rangle = \frac{2e}{h} \int_{-\infty}^{\infty} \tau(\epsilon) \left[ 1 + \frac{1}{e^\beta (\epsilon - \mu) + 1} - \frac{1}{e^\beta (\epsilon - \mu) + 1} \right] d\epsilon = \frac{2e}{h} \tau(\mu) \int_{-\infty}^{\infty} \left( \epsilon - \mu \right) \left[ 1 + \frac{1}{e^\beta (\epsilon - \mu) + 1} - \frac{1}{e^\beta (\epsilon - \mu) + 1} \right] d\epsilon = \frac{2e}{h} \tau(\mu) \frac{\pi^2 k^2 T^2}{3} \Delta T.
\]

This delta-T charge current becomes substantial at high temperatures; when $T = 30$ K, the electric current reaches at most $10^{-8}$ A, which is two orders of magnitude smaller than the value at $T = 300$ K.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{Delta-T noise in resonance tunneling junctions. (a) Lorentzian transmission function and the delta-T window for $T = 300$ K. (b) Current-$\Delta T$ characteristics at $T = 300$ K. (c) Excess noise as a function of $\Delta T$ for $T = 300$ K and (d) excess noise at $\Delta T = 30$ K. Calculations are based on Eq. \[13\] (full), constant transmission formula \[7\] (dashed), and the resonant-tunneling formula \[16\] (dashed-dotted). Simulations were performed with $\epsilon_d = 0.1$ eV, $\Gamma = 0.1$ eV, $T = 300$ K, unless otherwise specified.}
\end{figure}

\section*{V. SUMMARY}

It is often assumed that deviations from the standard shot noise formula, Eq. \[4\] indicate on the involvement of complex effects beyond those accounted for in the quantum coherent picture, e.g. electron heating or electron-phonon interactions. In contrast, our work here explicates that quantum coherent tunneling junctions can support ‘anomalous’ shot noise, which should be assessed before considering additional complex effects.

Revisiting the problem of quantum coherent transport in tunneling junctions, we derived expressions for the zero frequency current noise under large voltage bias or under a temperature difference. In such far-from-equilibrium situations, the transmission function cannot be assumed to be a constant, and one should take into account its...
variation with energy within the nonequilibrium window. Our main results are that the voltage-activated excess noise is a concave function of the scaled voltage, Eq. (11), and that it develops a cubic contribution at low temperature and high voltage, Eq. (13). We further demonstrated with simulations a highly nonlinear noise behavior, which was in accord with experimental observations, Fig. 4. Finally, we showed that the delta-T noise was well approximated by a quadratic formula, \( S_{\Delta T} \propto (\Delta T)^2 \), even when the resonance structure was accounted for. Our results further manifest that high voltage shot noise measurements can be used to uncover the structure of the transmission function at the Fermi energy.

We reiterate that quantum coherent transport can support rich phenomena far from equilibrium. For example, deviations from the so-called thermodynamic uncertainty relation [35], a bound relating dissipation to accuracy (fluctuations), were demonstrated in Ref. [36] within quantum coherent nanojunctions by considering situations that deviate from Markovianity.

Beyond the quantum coherent limit, electron correlations, electron-phonon interactions and other mechanisms for electron scattering should contribute to the appearance of anomalous noise as suggested in Refs. [21–23], and other studies. The explorations of such effects in single-molecule junctions, to reveal structural and dynamical information is left to future work.

Beyond shot noise, which is the second cumulant of charge fluctuations in steady state, a full counting statistics analysis recovers all cumulants, and it is useful for characterizing the transport process [37, 38]. In the context of molecular electronic junctions, understanding the information concealed in high order moments of the current [39–41] is left to future work.

ACKNOWLEDGMENTS

DS acknowledges fruitful discussions with Oren Tal and funding from the Natural Sciences and Engineering Research Council (NSERC) of Canada Discovery Grant and the Canada Chairs Program.

APPENDIX A: DERIVATION OF THE EQUILIBRIUM NOISE EQ. (6)

At equilibrium, \( T_L = T_R, \mu_L = \mu_R \), Eq. (3) reduces to

\[
S_1 + S_2 = \frac{4e^2}{\hbar} \int_{-\infty}^{\infty} d\epsilon \left( -2k_B T \frac{\partial f}{\partial \epsilon} \right) \tau(\epsilon).
\]  

We identify this contribution by \( S_{\Delta T}^{T,0} \), and it corresponds to the Johnson-Nyquist noise,

\[
S_{\Delta T}^{T,0} = 4k_B T G,
\]

generated by the thermal fluctuations of charge carriers in conductors at equilibrium. The linear response conductance is given by \( G = \frac{2e^2}{\hbar} \int d\epsilon \tau(\epsilon) \left( -\frac{\partial f}{\partial \epsilon} \right) \).

We further separately evaluate \( S_1 \) in Eq. (3) in the absence of bias voltage, for general \( T_L \) and \( T_R \). These expressions will be of use in Appendix C where we study the delta-T noise. Using exact identities for the Fermi function we get (omitting the prefactor \( 4e^2/\hbar \)),

\[
S_1 = \int_{-\infty}^{\infty} d\epsilon \left( -k_B T_L \frac{\partial f}{\partial \epsilon} - k_B T_R \frac{\partial f}{\partial \epsilon} \right) [\tau_0 + \tau'(\mu)(\epsilon - \mu)]^2.
\]

We evaluate the different terms and reach

\[
S_1 = \tau_0^2 k_B (T_L + T_R) + \int_{-\infty}^{\infty} d\epsilon \left( -k_B T_L \frac{\partial f}{\partial \epsilon} - k_B T_R \frac{\partial f}{\partial \epsilon} \right) 2\tau_0 \tau'(\mu)(\epsilon - \mu)
\]

\[
+ \int_{-\infty}^{\infty} d\epsilon \left( -k_B T_L \frac{\partial f}{\partial \epsilon} - k_B T_R \frac{\partial f}{\partial \epsilon} \right) [\tau'(\mu)]^2 (\epsilon - \mu)^2.
\]

Using integrals from Appendix E, we put together

\[
S_1 = 2G_0 \tau_0^2 k_B (T_L + T_R) + 2G_0 [\tau'(\mu)]^2 \left( \frac{\pi^2 k_B^2 T_L^3}{3} + \frac{\pi^2 k_B^2 T_R^3}{3} \right),
\]

where we re-instituted the prefactor \( 2G_0 = 4e^2/\hbar \). We define the averaged temperature, \( \bar{T} = (T_L + T_R)/2 \), and the temperature difference \( \Delta T = T_L - T_R \). Therefore, \( T_{L,R} = (\bar{T} \pm \Delta T/2) \), and \( T_L^3 + T_R^3 = 2\bar{T}^3 + 3\bar{T} \Delta T^2/2 \).
APPENDIX B: DERIVATION OF EQ. (11): VOLTAGE-ACTIVATED RESONANT-TUNNELING NOISE

We examine here the behavior of shot noise under arbitrarily large voltage; we assume that there is no applied temperature difference. We begin by evaluating $S_1$ in Eq. (3) using the expansion for the transmission function, Eq. [8]. For convenience, we omit the prefactor $\frac{A}{n}$, and re-install it only at the end of our derivation,

$$S_1 = \int_{-\infty}^{\infty} d\epsilon \left( -k_B T \frac{\partial f_L}{\partial \epsilon} - k_B T \frac{\partial f_R}{\partial \epsilon} \right) \times \left[ \tau_0 + \tau'(\mu)(\epsilon - \mu) \right]^2.$$  \hspace{1cm} (B1)

Here, $f_\nu = f(\epsilon, \nu, T)$, $\Delta \mu = \mu_L - \mu_R$, $2\mu = \mu_L + \mu_R$ and $T = T_L = T_R$. Explicitly,

$$S_1 = \int_{-\infty}^{\infty} d\epsilon \left( -k_B T \left[ \tau_0 \frac{\partial f_L}{\partial \epsilon} + 2\tau_0 \tau'(\mu)(\epsilon - \mu) \frac{\partial f_L}{\partial \epsilon} + [\tau'(\mu)]^2(\epsilon - \mu)^2 \frac{\partial f_L}{\partial \epsilon} \right] ight. + \left. (-k_B T) \left[ \tau_0 \frac{\partial f_R}{\partial \epsilon} + 2\tau_0 \tau'(\mu)(\epsilon - \mu) \frac{\partial f_R}{\partial \epsilon} + [\tau'(\mu)]^2(\epsilon - \mu)^2 \frac{\partial f_R}{\partial \epsilon} \right] \right).$$  \hspace{1cm} (B2)

We now evaluate the different terms,

$$I_1 \equiv \int_{-\infty}^{\infty} d\epsilon (-k_B T)^2 \tau_0^2 \frac{\partial f_L}{\partial \epsilon} = k_B^2 T \tau_0^2,$$

$$I_2 \equiv \int_{-\infty}^{\infty} d\epsilon (-k_B T)^2 2\tau_0 \tau'(\mu) \left( \epsilon - \left( \mu_L - \frac{\Delta \mu}{2} \right) \right) \frac{\partial f_L}{\partial \epsilon} = k_B T \tau_0 \tau'(\mu) \Delta \mu,$$

$$I_3 \equiv \int_{-\infty}^{\infty} d\epsilon (-k_B T)^2 [\tau'(\mu)]^2 \left( \epsilon - \left( \mu_L - \frac{\Delta \mu}{2} \right) \right) \frac{\partial f_L}{\partial \epsilon} = k_B T [\tau'(\mu)]^2 \frac{\pi^2 k_B^2 T^2}{3} + k_B T [\tau'(\mu)]^2 \left( \frac{\Delta \mu}{4} \right)^2.$$  \hspace{1cm} (B3)

Summing up these integrals, along with the corresponding contributions from the right side, we get

$$S_1 = 2k_B T \tau_0^2 + 2k_B T [\tau'(\mu)]^2 \left[ \frac{\pi^2 k_B^2 T^2}{3} + \left( \frac{\Delta \mu}{4} \right)^2 \right].$$  \hspace{1cm} (B4)

Next, we evaluate $S_2$ in Eq. (3). Under bias voltage it can be organized as

$$S_2 = \coth \left( \frac{\Delta \mu}{2k_B T} \right) \int_{-\infty}^{\infty} d\epsilon \left[ f_L(\epsilon) - f_R(\epsilon) \right] \tau_0 + \tau'(\mu)(\epsilon - \mu) \left[ 1 - \tau_0 - \tau'(\mu)(\epsilon - \mu) \right].$$  \hspace{1cm} (B5)

This integral can be evaluated exactly using the following relations,

$$I_4 \equiv \coth \left( \frac{\Delta \mu}{2k_B T} \right) \int_{-\infty}^{\infty} d\epsilon \left[ f_L(\epsilon) - f_R(\epsilon) \right] \tau_0 \left[ 1 - \tau_0 \right] \Delta \mu \coth \left( \frac{\Delta \mu}{2k_B T} \right),$$

$$I_5 \equiv \coth \left( \frac{\Delta \mu}{2k_B T} \right) \int_{-\infty}^{\infty} d\epsilon \left[ f_L(\epsilon) - f_R(\epsilon) \right] \left[ 1 - 2\tau_0 \right] \tau'(\mu)(\epsilon - \mu) = 0,$$

$$I_6 \equiv \coth \left( \frac{\Delta \mu}{2k_B T} \right) \int_{-\infty}^{\infty} d\epsilon \left[ f_L(\epsilon) - f_R(\epsilon) \right] [\tau'(\mu)]^2 (\epsilon - \mu)^2$$

$$= \coth \left( \frac{\Delta \mu}{2k_B T} \right) [\tau'(\mu)]^2 \left[ \Delta \mu \frac{\pi^2 k_B^2 T^2}{3} + \frac{1}{12} (\Delta \mu)^3 \right].$$  \hspace{1cm} (B6)

Overall, we get

$$S_2 = \tau_0 (1 - \tau_0) \Delta \mu \coth \left( \frac{\Delta \mu}{2k_B T} \right) - \coth \left( \frac{\Delta \mu}{2k_B T} \right) [\tau'(\mu)]^2 \left[ \Delta \mu \frac{\pi^2 k_B^2 T^2}{3} + \frac{1}{12} (\Delta \mu)^3 \right].$$  \hspace{1cm} (B7)
Summing up $S_1$ [Eq. (B4)] and $S_2$, we get the voltage-activated resonant-tunneling shot noise,
\[
S_{\Delta \mu} = 2k_BT\tau_0^2 + 2k_BT[\tau'(\mu)]^2 \left[ \frac{\pi^2 k_B^2 T^2}{3} + \frac{(\Delta \mu)^2}{4} \right] \\
+ \tau_0(1 - \tau_0)\Delta \mu \coth \left( \frac{\Delta \mu}{2k_BT} \right) - \coth \left( \frac{\Delta \mu}{2k_BT} \right) [\tau'(\mu)]^2 \left[ \Delta \mu \frac{\pi^2 k_B^2 T^2}{3} + \frac{1}{12}(\Delta \mu)^3 \right].
\] (B8)

Multiplying it by $2G_0 = \frac{4e^2}{h}$ we obtain Eq. (11).

**APPENDIX C: DERIVATION OF EQ. (16) FOR THE RESONANT-TUNNELING DELTA-T NOISE**

We study here the behavior of the shot noise at finite $\Delta T$, without applying a bias voltage. For convenience, we omit the prefactor $4e^2/h$. Eq. (5) is used inside Eq. (3), resulting in
\[
S_2 = \int_{-\infty}^{\infty} d\epsilon [f(\epsilon, \mu, T_L) - f(\epsilon, \mu, T_R)] \coth \left( \frac{\Delta \beta(\epsilon - \mu)}{2} \right) [\tau_0 + \tau'(\mu)(\epsilon - \mu)]
\]
\[
= \tau_0(1 - \tau_0)k_B \left[ (T_L + T_R) + \frac{(T_L - T_R)^2}{2T} \left( \frac{\pi^2}{9} - \frac{2}{3} \right) \right]
\]
\[
+ \int_{-\infty}^{\infty} d\epsilon [f(\epsilon, \mu, T_L) - f(\epsilon, \mu, T_R)] \coth \left( \frac{\Delta \beta(\epsilon - \mu)}{2} \right) (1 - 2\tau_0)\tau'(\mu)(\epsilon - \mu)
\]
\[
- \int_{-\infty}^{\infty} d\epsilon [f(\epsilon, \mu, T_L) - f(\epsilon, \mu, T_R)] \coth \left( \frac{\Delta \beta(\epsilon - \mu)}{2} \right) [\tau'(\mu)]^2(\epsilon - \mu)^2.
\] (C1)

Here, $\Delta \beta = \beta_R - \beta_L$. We Taylor-expand the two functions around the equilibrium (average) temperature up to $(\Delta T)^4$. These series will be used in Appendix D as well,
\[
f(\epsilon, \mu, T_L) - f(\epsilon, \mu, T_R) \approx \Delta T \frac{\partial f}{\partial T} + \frac{1}{24}(\Delta T)^3 \frac{\partial^3 f}{\partial T^3} + \frac{1}{16 \cdot 3!}(\Delta T)^5 \frac{\partial^5 f}{\partial T^5} + ...
\]
\[
\coth(\Delta \beta(\epsilon - \mu)/2) \approx \frac{2}{\Delta \beta(\epsilon - \mu)} + \frac{\Delta \beta(\epsilon - \mu)}{6} - \frac{(\Delta \beta)^3(\epsilon - \mu)^3}{360} + ...
\] (C2)

We note that
\[
\int_{-\infty}^{\infty} d\epsilon [f(\epsilon, \mu, T_L) - f(\epsilon, \mu, T_R)] \coth \left( \frac{\Delta \beta(\epsilon - \mu)}{2} \right)(\epsilon - \mu) = 0,
\] (C3)

since the integrand is a product of three odd functions. Next, we evaluate the last integral in Eq. (C1) to the quadratic order in $\Delta T$. From the Taylor expansion, we collect three contributions.
\[
\int_{-\infty}^{\infty} d\epsilon \frac{2}{\Delta \beta(\epsilon - \mu)} \Delta T \frac{\partial f}{\partial T}(\epsilon - \mu)^2 = \frac{\pi^2 k_B^2 T^2}{3} \left[ T^2 - \frac{(\Delta T)^2}{4} \right],
\]
\[
\int_{-\infty}^{\infty} d\epsilon \frac{2}{\Delta \beta(\epsilon - \mu)} \frac{1}{24}(\Delta T)^3 \frac{\partial^3 f}{\partial T^3}(\epsilon - \mu)^2 = 0,
\]
\[
\int_{-\infty}^{\infty} d\epsilon \frac{\Delta \beta(\epsilon - \mu)}{6} \Delta T \frac{\partial f}{\partial T}(\epsilon - \mu)^2 = \frac{7\pi^4}{90} k_B^2 T^2 (\Delta T)^2 + O(\Delta T^4).
\] (C4)

Note that $\Delta \beta = \frac{\Delta T}{T - \frac{\Delta T}{4}}$. Altogether, to the quadratic order we get,
\[
S_2 = \tau_0(1 - \tau_0)k_B \left[ (T_L + T_R) + \frac{(T_L - T_R)^2}{2T} \left( \frac{\pi^2}{9} - \frac{2}{3} \right) \right]
\]
\[
- [\tau'(\mu)]^2 \left[ \frac{2\pi^2 k_B^2 T^2}{3} + \left( \frac{7\pi^4}{90} - \frac{\pi^2}{6} \right) k_B^3 T (\Delta T)^2 \right].
\] (C5)

We re-install the factor $4e^2/h$ and add Eq. (A5),
\[
S_{\Delta T} = 4k_BT\tau_0 G_0 + G_0 k_B \tau_0 \frac{(\Delta T)^2}{T} \left( \frac{\pi^2}{9} - \frac{2}{3} \right)
\]
\[
- G_0[\tau'(\mu)]^2 \left( \frac{7\pi^4}{45} - \frac{4\pi^2}{3} \right) k_B^2 T (\Delta T)^2.
\] (C6)
This expression generalizes the results of Ref. [20]. It demonstrates that even when the transmission function varies with energy, \( \tau'(\mu) \neq 0 \), the delta-T noise scales as \( \Delta T^2 \). Unlike the zero order \( (\tau_0) \) contribution, the new term takes a negative sign. As well, the last term scales linearly with the averaged temperature, unlike the case of constant transmission. In Appendix D we furthermore evaluate the contribution of quartic terms \( (\Delta T)^4 \) to the resonant-tunneling delta-T noise.

**APPENDIX D: QUARTIC CONTRIBUTIONS TO THE RESONANT TUNNELING DELTA-T NOISE**

Complementing Appendix C, we evaluate here \( S_2 \) up to fourth order in \( \Delta T \). Some of the integrals were evaluated in Appendix C—but to the quadratic order. First, we consider the following integral,

\[
I_7 = \int_{-\infty}^{\infty} \frac{2}{\Delta \beta(\epsilon - \mu)} \Delta T \frac{\partial f}{\partial T}(\epsilon - \mu)^2 \frac{2\pi^2 k_B T}{3} \left[ T^2 - \frac{(\Delta T)^2}{4} \right].
\]

Recall that \( \Delta \beta = \beta_R - \beta_L \) and that \( \Delta T = T_L - T_R, \bar{T} = (T_L + T_R)/2 \). We further evaluate

\[
I_8 = \int_{-\infty}^{\infty} \frac{2}{\Delta \beta(\epsilon - \mu)} \Delta T \frac{\partial f}{\partial T}(\epsilon - \mu)^2 \frac{1}{24} (\Delta T)^2 \frac{\partial^3 f}{\partial T^3}(\epsilon - \mu)^2 = 0,
\]

\[
I_9 = \int_{-\infty}^{\infty} \Delta \beta(\epsilon - \mu) \frac{1}{6} \Delta T \frac{\partial f}{\partial T}(\epsilon - \mu)^2 \frac{7\pi^4 k_B T^3}{90} \left( \frac{(\Delta T)^2}{T^2} - \frac{1}{4} \right) = \frac{7\pi^4 k_B T^3 (\Delta T)^2}{90} \frac{[1 + (\Delta T)^2]}{4T^2} + O(\Delta T^6),
\]

and

\[
I_{10} = \int_{-\infty}^{\infty} \frac{\Delta \beta(\epsilon - \mu)}{6} (\Delta T)^2 \frac{\partial f}{\partial T}(\epsilon - \mu)^2 \frac{14\pi^4}{16} \frac{k_B T}{5} = \frac{14\pi^4}{16} \frac{k_B T}{5} \left( \frac{\Delta T}{T} \right)^3 + O(\Delta T^6),
\]

\[
I_{11} = \int_{-\infty}^{\infty} \frac{\Delta \beta(\epsilon - \mu)}{360} (\Delta T)^3 \frac{\partial f}{\partial T}(\epsilon - \mu)^2 \frac{31\pi^6 k_B T^6}{21} = \frac{31\pi^6 k_B T^6}{21} \left( \frac{\Delta T}{T} \right)^4 + O(\Delta T^6),
\]

\[
I_{12} = \int_{-\infty}^{\infty} \Delta \beta(\epsilon - \mu) \frac{1}{16 \times 5!} (\Delta T)^5 \frac{\partial^5 f}{\partial T^5}(\epsilon - \mu)^2 = 0.
\]

Summing up these terms up to fourth order in \( \Delta T \) we obtain

\[
S_2 = \tau_0(1 - \tau_0) k_B \left\{ \left[ (T_L + T_R) + \frac{(\Delta T)^2}{2T} \left( \frac{\pi^2}{9} - \frac{2}{3} \right) \right] + \frac{1}{T^3} \left( \frac{\pi^2}{72} - \frac{1}{24} + \frac{1}{40} - \frac{7}{15} \pi^4 \right) \right\}
- [\tau'(\mu)]^2 \left\{ \left[ \frac{2\pi^2 k_B T^5}{3} + \frac{(7\pi^4)}{90} - \frac{\pi^2}{6} \right] k_B \bar{T} (\Delta T)^2 \right\} + k_B \left[ \left( \frac{7\pi^4}{90} + \frac{1}{144} \right) \frac{1}{5} - \frac{1}{360} \pi^6 \right].
\]

We add \( S_1 \) from Eq. (A5) and furthermore evaluate the coefficients,

\[
S_{\Delta T} = 4k_B \bar{T} \tau_0 G_0 + G_0 k_B (1 - \tau_0) \left\{ 0.43 \frac{(\Delta T)^2}{T^2} - 0.012 \frac{(\Delta T)^4}{T^4} \right\}
- \tau_0 \left[ \tau'(\mu) \right]^2 k_B T^3 \left[ 1.99 \frac{(\Delta T)^2}{T^2} - 0.31 \frac{(\Delta T)^4}{T^4} \right].
\]
Only in the most extreme nonequilibrium case of $\Delta T = 2 \bar{T}$, the contribution of the quartic terms is within order of magnitude of the quadratic term—within the $\tau'$ correction. Therefore, we can safely ignore quartic contributions to the delta-T noise—as long as (D7) is valid. Back to Eq. (D7), we combine $S_1$ and $S_2$ up to second order in $\Delta T$, restore the factor $4e^2/\hbar$, and retrieve Eq. (16),

$$S_{\Delta T} = 4k_B\bar{T}G_0 + G_0k_B\tau_0(1 - \tau_0)\frac{(\Delta T)^2}{T}\left(\frac{\pi^2}{9} - \frac{2}{3}\right)$$

$$- G_0[\tau'(\mu)]^2\left(\frac{7\pi^4}{45} - \frac{4\pi^2}{3}\right)k_B^2(\Delta T)^2.$$  \hspace{1cm} (D9)

**APPENDIX E: USEFUL INTEGRALS**

Consider the Fermi-Dirac function $f(\epsilon) = \left[\frac{e^{\epsilon/T} + 1}{e^{\epsilon/T} - 1}\right]^{-1}$, the following relationship and integrals are useful to the evaluation of the shot noise,

$$f(\epsilon) [1 - f(\epsilon)] = k_B\bar{T}\left(-\frac{\partial f}{\partial \epsilon}\right), \quad \frac{\partial f}{\partial T} = -\frac{\epsilon}{T} \frac{\partial f}{\partial \epsilon} \hspace{1cm} (E1)$$

$$\int_{-\infty}^{\infty} d\epsilon \left(-\frac{\partial f}{\partial \epsilon}\right) = 1, \quad \int_{-\infty}^{\infty} d\epsilon \left(-\frac{\partial f}{\partial \epsilon}\right)^2 = 0, \hspace{1cm} (E2)$$

$$\int_{-\infty}^{\infty} d\epsilon \epsilon^2 \left(-\frac{\partial f}{\partial \epsilon}\right)^2 = \frac{\pi^2 k_B^2 T^2}{3}, \quad \int_{-\infty}^{\infty} d\epsilon \epsilon^4 \left(-\frac{\partial f}{\partial \epsilon}\right) = \frac{7\pi^4 k_B^4 T^4}{15}, \quad \int_{-\infty}^{\infty} d\epsilon \epsilon^6 \left(-\frac{\partial f}{\partial \epsilon}\right) = \frac{31\pi^6 k_B^6 T^6}{21}, \hspace{1cm} (E3)$$

$$\int_{-\infty}^{\infty} d\epsilon \epsilon^2 \left(-\frac{\partial f}{\partial \epsilon}\right)^2 = \frac{k_B T}{2}\left(\frac{\pi^2}{9} - \frac{2}{3}\right), \hspace{1cm} (E4)$$

$$\int_{-\infty}^{\infty} d\epsilon \frac{1}{\epsilon} \left(\frac{\partial^3 f}{\partial T^3}\right) = \frac{2}{T^3}, \quad \int_{-\infty}^{\infty} d\epsilon \frac{1}{\epsilon} \left(\frac{\partial^5 f}{\partial T^5}\right) = \frac{24}{T^5}, \hspace{1cm} (E5)$$

$$\int_{-\infty}^{\infty} d\epsilon \epsilon^3 \left(\frac{\partial^3 f}{\partial T^3}\right) = 0, \quad \int_{-\infty}^{\infty} d\epsilon \epsilon^5 \left(\frac{\partial^5 f}{\partial T^5}\right) = 0, \hspace{1cm} (E6)$$

$$\int_{-\infty}^{\infty} d\epsilon \epsilon^3 \left(\frac{\partial^3 f}{\partial T^3}\right) = \frac{14\pi^4 k_B^4 T^4}{5}. \hspace{1cm} (E7)$$

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