Probing Maxwell's Demon with a Nanoscale Thermometer

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ABSTRACT A precise definition for a quantum electron thermometer is given, as an electron reservoir coupled locally (e.g., by tunneling) to a sample, and brought into electrical and thermal equilibrium with it. A realistic model of a scanning thermal microscope with atomic resolution is then developed, including the effect of thermal coupling of the probe to the ambient environment. We show that the temperatures of individual atomic orbitals or bonds in a conjugated molecule with a temperature gradient across it exhibit quantum oscillations, whose origin can be traced to a realization of Maxwell’s demon at the single-molecule level. These oscillations may be understood in terms of the rules of covalence describing bonding in π-electron systems. Fourier’s law of heat conduction is recovered as the resolution of the temperature probe is reduced, indicating that the macroscopic law emerges as a consequence of coarse graining.

Keywords: quantum thermometer · scanning thermal microscope (SThM) · three-terminal heat transport theory · definition of temperature · single-molecule heat transport · thermoelectric effects · Fourier’s law · rules of covalence

Recent advances in thermal microscopy1–5 have opened the door to understanding nonequilibrium thermodynamics at the nanoscale. The nonequilibrium temperature distribution in a quantum system subject to a thermal or electric gradient can now be probed experimentally, raising a number of fundamental questions: Can significant temperature variations occur across individual atoms or molecules without violating the uncertainty principle? How are the electronic and lattice temperatures related in a nanostructure out of thermal equilibrium? How does the classical Fourier law of heat conduction emerge6,7 from this quantum behavior in the macroscopic limit?

In order to address these questions theoretically, a definition of a nanoscale thermometer that is both realistic and mathematically rigorous is needed. According to the principles of thermodynamics, a thermometer is a small system (probe) with some readily identifiable temperature-dependent property that can be brought into thermal equilibrium with the system of interest (sample). Once thermal equilibrium is established, the net heat current between probe and sample vanishes,8–10 and the resulting temperature of the probe constitutes a measurement of the sample temperature. High spatial and thermal resolution require that the thermal coupling between probe and sample is local8 and that the coupling between the probe and the ambient environment is small,2 respectively.

It should be emphasized that, out of equilibrium, the temperature distributions of different microscopic degrees of freedom (e.g., electrons and phonons) do not, in general, coincide, so that one has to distinguish between measurements of the electron temperature8,11 and the lattice temperature.10,12 This distinction is particularly acute in the extreme limit of elastic quantum transport,13 where electron and phonon temperatures are completely decoupled.

In this article, we develop a realistic model of a scanning thermal microscope (SThM) operating in the tunneling regime in ultra-high vacuum, where the vacuum tunneling gap ensures that phonon heat conduction to the probe is negligible. Since electrons carry both charge and heat, an additional condition is necessary to define an electron thermometer. We proceed by noting that, as a practical matter, in order to reduce the thermal coupling of the thermometer to the...
ambient environment, it should form an open electrical circuit (or have very high impedance to ground). This ensures that, in addition to the heat current, the electrical current between sample and probe vanishes. This second condition is also necessary to ensure the thermometer is in local equilibrium with the sample. An electron thermometer is thus defined as an electron reservoir whose temperature is fixed by the conditions of electric and thermal equilibrium with the sample:

\[ I^{(v)}_p = 0, \; v = 0, 1 \]  \hspace{1cm} (1)

where \( I_p \equiv -eI^{(0)}_p \) and \( I^{(0)}_p \) are the electric current and heat current, respectively, flowing into the probe. In an ideal measurement, the sample would be the sole source of charge and heat flowing into the probe, but we also consider nonideal measurements, where there is an additional thermal coupling to the ambient environment. In practice, this coupling plays a crucial role in limiting the resolution of temperature measurements.\(^4\)

In a measurement of the temperature distribution in a conductor subject to thermal and/or electric gradients, the electron thermometer thus serves as an open third terminal in a three-terminal thermoelectric circuit, a generalization of Büttiker’s voltage probe concept\(^14\) (see Figure 1). Note that the conditions of eq 1 allow a local temperature to be defined under general thermoelectric bias conditions, relevant for the analysis of nonequilibrium thermoelectric device performance.\(^15\)–\(^18\)

Previous theoretical analyses of quantum electron thermometers either completely neglected thermoelectric effects\(^8\),\(^9\),\(^19\) or considered the measurement scenario of eq 1 as only one of several possible cases,\(^20\)–\(^23\) without giving definitive arguments for one case over the others. The subtle definition of local temperature given in ref 11 (thermometer causes minimal perturbation of system dynamics), on the other hand, may capture the spirit of our two separate conditions, at some level. A recent review of the topic is given in ref 24. To our knowledge, a theoretical analysis of the effect of finite coupling of the temperature probe to the ambient environment has not previously been undertaken.

Using our model of a nanoscale electron thermometer, we investigate the nonequilibrium temperature distributions in single-molecule junctions subject to a thermal gradient. Quantum temperature oscillations analogous to those predicted in one-dimensional systems\(^11\) are predicted in molecular junctions for several different conjugated organic molecules and are explained in terms of the rules of covalence describing bonding in \( \pi \)-conjugated systems. In terms of directing the flow of heat, the rules of covalence can be seen as an embodiment of Maxwell’s demon at the single-molecule level.

\[ T^{(v)}_p = 0 \; \text{for } v \in \{0, 1\} \]

\[ \mu_1, T_1 \]

\[ \mu_2, T_2 \]

\[ \mu_p, T_p \]

\[ \begin{array}{c}
\mu_1, T_1 \\
\mu_2, T_2 \\
\mu_p, T_p \\
\end{array} \]

Figure 1. Schematic representation of a temperature probe as an open third terminal of a thermoelectric circuit.

It has been argued that in some systems quantum temperature oscillations can be washed out by either dephasing\(^6\) or disorder,\(^7\) leading to restoration of Fourier’s classical law of heat conduction. However, in molecular junctions the required scattering would be so strong as to dissociate the molecule. We investigate the effect of finite spatial resolution on the nonequilibrium temperature distribution and find that Fourier’s law emerges naturally as a consequence of coarse-graining of the measured temperature distribution. Thus our resolution of the apparent contradiction between Fourier’s macroscopic law of heat conduction and the predicted nonmonotonic temperature variations at the nanoscale is that the quantum temperature oscillations are really there, provided the temperature measurement is carried out with sufficient resolution to observe them, but that Fourier’s law emerges naturally when the resolution of the thermometer is reduced.

This paper is organized as follows: We first derive a general linear-response formula for an electron thermometer. A realistic model of a scanning thermal microscope with sub-nanometer resolution is then developed, including a discussion of thermal coupling of the probe to the environment. Finally, results for the nonequilibrium temperature distributions in several single-molecule junctions subject to a thermal gradient are presented, and the implications of our findings are discussed.

RESULTS AND DISCUSSION

Electronic Temperature Probe. Consider a general system with \( M \) electrical contacts. Each contact \( \alpha \) is connected to a reservoir at temperature \( T_\alpha \) and electrochemical potential \( \mu_\alpha \). In linear response, the electrical current \(-eI^{(0)}_\alpha\) and heat current \( I^{(1)}_\alpha\) flowing into reservoir \( \alpha \) may be expressed as

\[ I^{(\nu)}_\alpha = \sum_{\beta=1}^{M} \left[ r^{(\nu)}_{\alpha \beta} (\mu_\beta - \mu_\alpha) + \frac{\gamma^{(\nu+1)}_{\alpha \beta}}{T} (T_\beta - T_\alpha) \right] \]  \hspace{1cm} (2)

where \( r^{(\nu)}_{\alpha \beta} \) is an Onsager linear-response coefficient. Equation 2 is a completely general linear-response formula and applies to macroscopic systems, mesoscopic systems, nanostructures, etc., including electrons, phonons, and all other degrees of freedom, with arbitrary interactions between them. For a discussion of this general linear-response formula applied to bulk systems, see ref 25.
In this article, we consider systems driven out of equilibrium by a temperature gradient between reservoirs 1 and 2. Thermoelectric effects are included, so the chemical potentials of the various reservoirs may differ. We consider pure thermal circuits (i.e., open electrical circuits), for which $\Delta u_{\alpha}^{(0)} = 0 \forall \alpha$. These conditions may be used to eliminate the chemical potentials $\mu_{\alpha}$ from eq 2, leading to a simpler formula for the heat currents:

$$I_{\alpha}^{(1)} = \frac{1}{\beta} \sum_{\beta=1}^{2} \kappa_{\alpha\beta}(T_{\beta} - T_{\alpha})$$

(3)

In the absence of an external magnetic field $f_{\alpha}^{(0)} = f_{\alpha}^{(1)}$ and the three-terminal thermal conductances are given by

$$\kappa_{\alpha\beta} = \frac{1}{T} \left[ f_{\alpha}^{(2)} - \frac{f_{\alpha}^{(1)} f_{\alpha}^{(1)}}{f_{\beta}^{(1)}} \right]$$

(4)

with

$$f_{\alpha}^{(0)} = f_{\alpha}^{(0)} + f_{\alpha}^{(1)} f_{\alpha}^{(1)}$$

(5)

and

$$f_{\alpha}^{(1)} = f_{\alpha}^{(0)} + f_{\alpha}^{(1)} f_{\alpha}^{(1)} + f_{\alpha}^{(1)} f_{\alpha}^{(2)}$$

(6)

An equivalent circuit for $f_{\alpha}^{(0)}$ and $f_{\alpha}^{(1)}$ is given in Figure 2.

The first line of eq 4 resembles the familiar two-terminal thermal conductance,

$$\kappa_{\alpha\beta} = \frac{1}{T} \left[ f_{\alpha}^{(2)} - f_{\alpha}^{(1)} f_{\alpha}^{(1)} \right]$$

with $f_{\alpha}^{(0)}$ replaced by eq 5. Since $f_{\alpha}^{(0)}$ is usually the dominant term, $\kappa_{\alpha\beta}$ is often comparable to the two-terminal form $\kappa_{\alpha\beta}$ (cf. Figure 6).

However, the discrepancy is sizable in some cases. Although it might be tempting to interpret the second line in eq 4 as a nonlocal quantum correction to the thermal conductance, it should be emphasized that this is a generic three-terminal thermoelectric effect that arises in bulk systems as well as nanostructures.

**Temperature Measurement.** In addition to the coupling of the temperature probe to the system of interest, we assume the probe also has a small thermal coupling $\kappa_{p0}$ to the environment at temperature $T_{0}$. The environment could be, for example, the blackbody radiation or gaseous atmosphere surrounding the circuit or the cantilever/driver on which the temperature probe is mounted. The heat current flowing from the environment into the probe must be added to eq 3 to determine the total heat current:

$$I_{p}^{2} = \frac{2}{\beta} \sum_{\beta=1}^{2} \kappa_{\alpha\beta}(T_{\beta} - T_{\alpha}) + \kappa_{p0}(T_{0} - T_{p})$$

(7)

Thermal coupling to the environment is important when the coupling to the system is weak, and it is a limiting factor in the thermal resolution of any temperature probe. The environment is effectively a fourth terminal in the thermoelectric circuit; however, we consider only thermal coupling of the probe to the environment, so the thermal conductances $\kappa_{p1}, \kappa_{p2}$ in eq 7 have the three-terminal form (eq 4). Solving eqs 1 and 7 for the temperature, we find

$$T_{p} = \frac{\kappa_{p1}T_{1} + \kappa_{p2}T_{2} + \kappa_{p0}T_{0}}{\kappa_{p1} + \kappa_{p2} + \kappa_{p0}}$$

(8)

for a probe in thermal and electrical equilibrium with, and coupled locally to, a system of interest. Experimentally, the reduction of the thermal response of the probe at finite $\kappa_{p0}$ is characterized by the sensitivity:

$$S = \frac{\partial T_{s}}{\partial T_{s}} = \frac{\kappa_{ps}}{\kappa_{ps} + \kappa_{p0}}$$

(9)

where $T_{s}$ is the sample temperature and $\kappa_{ps} = \kappa_{p1} + \kappa_{p2}$ is the total thermal conductance between the probe and the sample. Equation 9 follows directly from eq 8 with $T_{1} = T_{2} = T_{p}$.

Equations 4 and 8 provide a general definition of an electron thermometer coupled to a system with a temperature gradient across it, in the linear response regime. Equation 8 can be rewritten in the following instructive form:

$$T_{p} = T_{0} + S(\bar{T} - T_{0}) + S \Delta T/2$$

(10)

where $T_{1} = \bar{T} + \Delta T/2, T_{2} = \bar{T} - \Delta T/2, S$ is the sensitivity, and $C$ is the contrast defined by

$$C = \frac{\kappa_{p1} - \kappa_{p2}}{\kappa_{p1} + \kappa_{p2} + \kappa_{p0}}$$

(11)

For the case of a symmetric thermal bias ($\bar{T} = T_{0}$), $T_{p} - T_{0}$ is proportional to the contrast, and the second term on the right-hand side of eq 10 is zero. A symmetric thermal bias is of particular interest from a theoretical point of view, but may be difficult to realize in the laboratory, where it is common to heat one electrode and keep the other electrode at ambient temperature; $T_{1} = T_{0} + \Delta T, T_{2} = T_{0}$. Here we point out that it is possible to extract the quantity of theoretical interest $C$ (i.e., quantum temperature oscillations) from a
sequence of two measurements: (a) where both electrodes are heated, \( T_1 = T_2 = T_0 + \Delta T \), yielding \( T_p \) \( = T_0 + S \Delta T \); and (b) where only one electrode is heated, \( T_1 = T_0 + \Delta T \), \( T_2 = T_0 \) yielding \( T_p \) \( = T_0 + S \Delta T /2 + C \Delta T /2 \). Then \( 2T_p - T_0 = T_0 + C \Delta T \). In the remainder of this article, we focus on the case of a symmetric thermal bias. Explicit results for a junction where one electrode is heated and the other is kept at ambient temperature are given in the Supporting Information.

**Quantum Electron Thermometer.** We consider nanoscale junctions with weak electron–phonon coupling operating near room temperature. Under linear-response conditions, electron–phonon interactions and inelastic phonon scattering are weak in such systems, and the indirect phonon contributions to \( \gamma_{\alpha \beta} \) and \( \gamma_{\alpha \beta}^{(1)} \) can be neglected, while the direct phonon contribution to \( \gamma_{\alpha \beta}^{(1)} \) is negligible due to the vacuum tunneling gap. The linear response coefficients needed to evaluate eq 8 may thus be calculated using elastic electron transport theory.\(^{27,26,27}\)

\[
\gamma_{\alpha \beta}^{(1)} = \frac{1}{\hbar} \int dE \left( \mu_0 - \mu_n \right) \Gamma_{\alpha \beta}(E) \left( \frac{\partial f_n(E)}{\partial E} \right) \tag{12}
\]

where \( f_n \) is the equilibrium Fermi–Dirac distribution of the electrodes at chemical potential \( \mu_0 \) and temperature \( T_0 \). The transmission function may be expressed as\(^{3,28}\)

\[
\Gamma_{\alpha \beta}(E) = \text{Tr}[\Gamma^{\alpha}(E) G(E) \Gamma^{\beta}(E) G^\dagger(E)] \tag{13}
\]

where \( \Gamma^{\alpha}(E) \) is the tunneling-width matrix for lead \( \alpha \) and \( G(E) \) is the retarded Green’s function of the junction.

**SPM-Based Temperature Probe of a Single-Molecule Junction.** As an electron thermometer with atomic-scale resolution, we propose using a scanning probe microscope (SPM) with an atomically sharp conducting tip mounted on an insulating piezo actuator designed to minimize the thermal coupling to the environment. The tip could serve, for example, as a bolometer or thermocouple,\(^4\) and its temperature could be read out electrically using ultrafine shielded wiring. The proposed setup is essentially a nanoscale version of the commercially available STHM and is analogous to the ground-breaking STHM with 10 nm resolution developed by Kim et al.,\(^4\) but operating in the tunneling regime rather than the contact regime.

Such an atomic-resolution electron thermometer could be used to probe the local temperature distribution in a variety of nanostructures/mesoscopic systems out of equilibrium. In the following, we focus on the specific example of a single-molecule junction (SMJ) subject to a temperature gradient, with no electrical current flowing. In particular, we consider junctions containing conjugated organic molecules, the relevant electronic states of which are determined by the \( \pi \)-orbitals. We consider transition metal tips, where tunneling is dominated by the d-like orbitals of the apex atom.\(^{29}\)

The tunnel coupling between the tip of the electronic temperature probe and the \( \pi \)-system of the molecule is described by the tunneling-width matrix.\(^{29,30}\)

\[
\Gamma_{\alpha m}(E) = 2\pi V_n V_m \rho_\alpha(E) \tag{14}
\]

where \( n \) and \( m \) label \( \pi \)-orbitals of the molecule, \( \rho_\alpha(E) \) is the local density of states on the apex atom of the probe, and \( V_n \) is the tunneling matrix element between the evanescent tip wave function and orbital \( m \) of the molecule. Since the temperature probe is in the tunneling regime, and not the contact regime, the phonon contribution to the transport vanishes; heat is exchanged between system and probe only via the electron tunneling characterized by \( \Gamma^p \).

![Figure 3. Calculated spatial map of \( \text{Tr}[\Gamma^p] \) for a Pt electron thermometer scanned 3.5 Å above the plane of a benzene molecule and a schematic representation of a para-benzenedithiol (1,4BDT) junction. Peak values of \( \text{Tr}[\Gamma^p] \) \( \approx \) 16.6 meV correspond to the centers of the carbon atoms, which are numbered in black. The sulfur and gold atoms were drawn using their covalent radii of 102 and 134 pm, respectively.](image)

In Figure 3, the trace of \( \Gamma^{\alpha} \) is shown for a Pt temperature probe held 3.5 Å above the plane of a Au–[1,4]benzenedithiol–Au (1,4BDT) molecular junction. A schematic of the [1,4]BDT junction is also shown, with sulfur and gold atoms drawn to scale using their covalent radii of 102 and 134 pm, respectively. Peaks in \( \text{Tr}[\Gamma^p] \) correspond to the locations of carbon \( \pi \)-orbitals, labeled with black numbers. \( \Gamma^p \) determines the tunneling transmission probabilities through eq 13 and the thermoelectric response coefficients through eq 12. These in turn determine the measured temperature through eqs 4 and 8.

The density of states (DOS) of the Au–para BDT–Au junction is shown in Figure 4, simulated using our many-body theory including the electrostatic influence of the thiol end groups. Our many-body theory accurately reproduces the fundamental gap of gas-phase benzene (\( \sim \)10.4 eV), allowing us to unambiguously determine the energy-level alignment between the electrodes and molecule. Transport occurs within the HOMO–LUMO gap, but is dominated by the...
In all benzene simulations including the $e_{2}$ and LUMO resonances, calculated using many-body theory and linear-response conductance measurements. The blue line indicates the Pt probe’s Fermi energy, $E_{F} = -5.53$ eV, averaged over the $[110]$, $[111]$, $[320]$, and $[331]$ crystal planes.\textsuperscript{31}

HOMO resonance. This is true for all of the molecular junctions considered in this article.

**Coupling to the Environment.** The thermal coupling $\kappa_{p0}$ of the temperature probe to the ambient environment places stringent limits on the thermal resolution of a STHM.\textsuperscript{2,4} An accurate temperature measurement requires either sensitivity $S \approx 1$ ($\kappa_{p0} \gg \kappa_{s0}$), so that $T_{p} \approx T_{s}$, or $S \approx \text{const}$, so that it may be taken as a constant correction factor.\textsuperscript{5} In the tunneling regime investigated in the present work, we shall see that $S \neq \text{const}$, so that accurate temperature measurements require high sensitivity. Nonetheless, we demonstrate that the qualitative features of the nonequilibrium temperature distribution can be faithfully captured even when $S \ll 1$.

In the simulations presented here, we consider both a very weak environmental coupling ($\kappa_{p0} = 10^{-4} \kappa_{s0}$, for which $S \approx 1$ over much of the sample) and a fairly strong environmental coupling ($\kappa_{p0} = 10 \kappa_{s0}$ for which $S \ll 1$). Here $\kappa_{s0} = (\pi T / 3)(k_{B}^{2} T / h) = 2.84 \times 10^{-10}$ W/K is the thermal conductance quantum.\textsuperscript{31,32} For comparison, the UHV SThM of Kim et al.\textsuperscript{4} recently achieved $\kappa_{p0} \approx 700 \kappa_{s0}$. Observation of the quantum effects on the nonequilibrium temperature distribution predicted theoretically\textsuperscript{11} and investigated in this work would require a significant reduction of $\kappa_{p0}$ compared to the current experimental state of the art, not unlike the push to observe quantum effects in nanofabricated oscillators.\textsuperscript{35}

There are both practical and fundamental limits on $\kappa_{p0}$. In a gaseous atmosphere, STHM resolution is limited by convection.\textsuperscript{2} In the UHV SThM of ref 4, $\kappa_{p0}$ is dominated by conduction through the cantilever upon which the temperature probe is mounted. A fundamental limitation is radiative coupling to the ambient blackbody environment, for which

$$\frac{\kappa_{p0}}{\kappa_{s0}} = \frac{2 \pi \epsilon A}{5} \left(\frac{k_{B} T_{0}}{\hbar c}\right)^{2} \frac{10^{-300 K} \text{m}^{3}}{10 \mu m^{3}}$$

The conducting tip of the temperature probe must thus have linear dimensions $R \leq 10 \mu m$ in order to resolve quantum effects at room temperature. A conducting tip of small volume will also ensure rapid equilibration of the probe with the sample (see Methods section).

We do not include the direct radiative contribution to $\kappa_{p1}$ and $\kappa_{p2}$. Since the separation between electrodes 1 and 2 is much less than the photon thermal wavelength, we consider that blackbody radiation from the two electrodes contributes to a common ambient environment at temperature $T = T_{0}$. Near-field effects may lead to an increase of $\kappa_{s0}$ over the value given by eq 15, but the contribution to $\kappa_{p0}$ due to near-field radiation is nonetheless estimated to be quite small\textsuperscript{1} and slowly varying spatially compared to electronic processes. We do not consider radiative coupling of the probe to the molecule itself due to the strong quantum suppression of radiative heat transfer for structures smaller than the thermal wavelength.\textsuperscript{36}

**Nonequilibrium Temperature Distributions.** In this section, we investigate the spatial temperature profiles for three Au--benzenedithiol--Au (BDT) junction geometries, a linear $[1,6]$hexatrieneedithiol junction, and a polycyclic $[2,7]$pyrenedithiol junction. The BDT and hexatriene SMJ calculations were performed using a molecular Dyson equation many-body transport theory\textsuperscript{13} in which the molecular $\pi$-system is solved exactly, including all charge and excited states, and the lead-molecule tunneling is treated to infinite order (see Methods section). The transport calculations for the pyrene junction were performed using Hückel theory (see Supporting Information). In all cases, the ambient temperature is taken as $T_{0} = 300$ K.

**Benzenedithiol Junctions.** We investigate the temperature distributions for three Au--benzenedithiol--Au (BDT) junction geometries: the “para” $[1,4]$BDT junction, shown schematically along with the trace of the lead-molecule coupling matrix in Figure 3, the “ortho” $[1,2]$BDT junction, and the “meta” $[1,3]$BDT junction. The calculated spatial temperature distribution for each junction configuration is shown in Figure 5, for both weak and strong environmental couplings, with $T_{1} = 325$ K and $T_{2} = 275$ K. The figure illustrates quantum oscillations of the local temperature near the molecules, which are clearly resolvable using our model of a nanoscale electron thermometer. In each junction, the $\pi$-orbitals of the molecule have a characteristic temperature different from that of its nearest neighbors. For instance, in the para junction orbitals 2 and 6 are hot, orbitals 3 and 5 are cold, while orbitals 1 and 4, directly connected to the hot and cold
proximal to the hot and cold electrodes, respectively. For these pro-
arising from o-
structures shown in Figure 7. (e, f) Temperature distribution of the meta junction exhibits well-de-
temperature are clearly visible in the vicinity of the molecule, which can be explained in terms of the Kekulé contributing
for weak (upper panels) and strong (lower panels) SThM-environment coupling strengths. (a
10
ε
π
β
κ
p
β
κ
p
\kappa_0 = 10^{-4} \kappa_0 
κ
p
0 = 10 \kappa_0

The sulfur linker atoms are included in the transport calculations and are shown as red and blue circles, indicating the contacts
to electrode
the probe is in the ortho or para con
Electrode. Figure 6a indicates that
thermal correction to the thermal conductance
between the probe and the hot electrode is nearly zero when the probe is in the meta
configuration relative to electrode
β
κ
p
β
κ
p
\kappa_0 = 10^{-4} \kappa_0
κ
p
0 = 10 \kappa_0

When \kappa_{p1} \gg \kappa_{p2}, eq 8 implies the probe will
measure a temperature near \( T_1 \), and vice versa when \kappa_{p1} \ll \kappa_{p2} provided the coupling to the environment
is not too large. On the other hand, the probe will
measure a temperature near \( T_0 \) if \kappa_{p1} \approx \kappa_{p2}. Comparing
the para temperature profile shown in Figure 5a,b to Figure 6, one sees that \( \pi \)-orbitals 2 and 6 are hot
because when the SThM is coupled locally to them it is
in an ortho configuration relative to the hot electrode
and a meta configuration relative to the cold electrode,
and \( \kappa_{ortho} \gg \kappa_{meta} \). Orbitals 3 and 5 are cold by
symmetry. On the other hand, orbitals 1 and 4 have
intermediate temperatures since \( \kappa_{p1} \approx \kappa_{p2} \) when the
SThM is in a para configuration relative to one electrode
and proximal to the other.

The quantum temperature oscillations in the para
junction can also be understood in terms of the rules of
covalence in conjugated systems. Figure 7 shows the
Kekulé contributing structures illustrating charge
transfer from an electrode E to a benzene molecule.
Considering both hot and cold electrodes, the rules of
covalence dictate that electrons from the hot electrode
are available to tunnel onto the temperature probe
when it is coupled locally to orbital 2, 4, or 6, while
electrons from the cold electrode are available to
tunnel when the probe is near orbital 1, 3, or 5. In
addition, electrons from the hot electrode are available
to tunnel onto the temperature probe when it is near

Figure 5. Calculated spatial temperature distributions of para ([1,4]BDT), ortho ([1,2]BDT), and meta ([1,3]BDT) junctions
measured by a Pt SThM scanned 3.5 Å above the plane of carbon nuclei with \( T_1 = 325 \text{ K} \) and \( T_2 = 275 \text{ K} \). Each junction is shown
for weak (upper panels) and strong (lower panels) SThM-environment coupling strengths. (a–d) Quantum oscillations of the
temperature are clearly visible in the vicinity of the molecule, which can be explained in terms of the Kekulé contributing
structures shown in Figure 7. (e, f) Temperature distribution of the meta junction exhibits well-defined “bond temperatures”
 arising from off-diagonal contributions to the thermal transport, in addition to the “orbital temperatures” of orbitals 1 and 3
proximal to the hot and cold electrodes, respectively. For these profiles, \( \frac{\Delta T}{C_0} \approx 0.9 \) for \( \kappa_{p0} = 10^{-9} \kappa_0 \) and \( \frac{\Delta T}{C_0} \approx 1.1 \times 10^{-5} \) for \( \kappa_{p0} = 10 \kappa_0 \), indicating temperature oscillations can be observed even with small sensitivities (see Methods section).
The sulfur linker atoms are included in the transport calculations and are shown as red and blue circles, indicating the contacts
to the hot and cold leads, respectively.

In order to understand the temperature oscillations
shown in Figure 5, it is useful to consider the thermal conductance \( \kappa_{p1} \) between the probe and the hot
electrode. Figure 6a indicates that \( \kappa_{p1} \) is large when the probe is in the ortho or para configuration relative
to electrode \( \beta \), as well as when it is proximal to the
\( \pi \)-orbital directly coupled to the electrode. However, \( \kappa_{p1} \) is nearly zero when the probe is in the meta
configuration relative to electrode \( \beta \). The three-
terminal correction to the thermal conductance \( \Delta \kappa_{p1} \) is plotted in Figure 6b, which indicates that three-
terminal thermoelectric effects lead to a sizable relative
correction to the thermal conductance between the
probe and the electrode in the meta configuration, but
are otherwise small.
orbital 1, which is proximal to the hot electrode, while electrons from the cold electrode are available to tunnel onto the temperature probe when it is near orbital 4, which is proximal to the cold electrode. Orbitals 2 and 6 thus appear hot, orbitals 3 and 5 appear cold, while orbitals 1 and 4 should exhibit intermediate temperatures by this argument.

The calculated temperature distribution of an ortho BDT junction is shown in Figure 5c,d, measured under the same conditions as the para junctions. The Kekulé contributing structures illustrated in Figure 7 dictate that lone pairs from the hot electrode may tunnel to orbital 2, 4, or 6, and lone pairs from the cold electrode may tunnel to orbital 1, 3, or 5. Taking into account that orbitals 1 and 2 are also proximal to the linker groups binding the molecule to the hot and cold electrodes, respectively, and thus exhibit intermediate temperatures, the rules of covalence dictate that orbitals 4 and 6 appear hot, while orbitals 3 and 5 appear cold, in complete agreement with the calculated temperature distribution.

For the para and ortho junctions the rules of covalence act essentially like a Maxwell demon, in that they selectively permit electrons from the hot or cold reservoir to tunnel onto the probe when it is at specific locations near the molecule and block electrons from the other reservoir. The situation is analogous to the “temperature demon”, wherein a tiny being controls the transfer of gas molecules between two containers, allowing only fast-moving molecules to flow from container 1 to container 2 and only slow-moving molecules to flow in the opposite sense, leading to a violation of the second law of thermodynamics. Rather than gas molecules, the present case involves electrons, while the molecular junction and metal tip of the SThM represent containers 1 and 2, respectively. When the temperature probe is at one of the hot spots in Figure 5, the rules of covalence do not allow electrons within the molecule, chosen at random, to tunnel onto the tip, but only electrons with an energy distribution characteristic of the hot reservoir; a distribution hotter than the mean temperature of the molecule.

As the probe equilibrates at such a hot spot, heat is thus transferred from the molecule to the probe, whose temperature is higher than the mean temperature of the molecule.

The question might arise whether the actions of this would-be Maxwell demon could lead to a violation of the second law of thermodynamics, as Maxwell originally hypothesized. However, in this case there is no violation of the second law, because electrons within the molecule “remember” which electrode they came from. There is no “mixing” of the hot and cold electrons in the absence of inelastic scattering, which is strongly suppressed compared to elastic processes in these junctions at room temperature.
The observed temperature oscillations can be explained using the resonance contributing structures shown in Figure 9. The calculated temperature distribution of a meta BDT junction is shown in Figure 8. The observed temperature oscillations are no longer resolved, and the underlying temperature gradient appears. In the rightmost panel, quantum temperature oscillations are no longer resolved, and the temperature distribution resembles a thermal dipole. Similar results were obtained for a variety of molecular junctions, suggesting that a classical temperature distribution consistent with Fourier’s law of heat transfer from an electrode E onto the molecule are shown in Figure 9. As in the case of the para and ortho BDT junctions, the rules of covalence are unambiguous and predict alternating hot and cold temperatures for the \( \pi \)-orbitals along the length of the molecule, with intermediate temperatures for the end orbitals proximal to the two electrodes, consistent with the calculated temperature distribution.

**[2,7]Pyrenedithiol Junction.** As a final example, we consider the effects of finite spatial resolution on the measured temperature distribution of a polycyclic [2,7]pyrenedithiol-Au junction. The temperature distribution was calculated for three different values of the SThM spatial resolution in the three panels of Figure 10: The leftmost panel shows the maximum spatial resolution under the specifications of a hypothetical SThM described in Figure 5. The middle and rightmost panels show the measured temperature distributions with reduced spatial resolution obtained by convolving the tip-sample tunnel-coupling \( \Gamma \) with Gaussian distributions with standard deviations of \( \sigma = 0.5 \) and 1.0 Å, respectively (full resolution corresponds to \( \sigma = 0 \)). Many-body transport calculations for this larger molecule are currently computationally intractable, so we have utilized Hückel theory to describe the molecular electronic structure (see Supporting Information).

The leftmost panel of Figure 10 shows a complex interference pattern of hot and cold regions with a symmetry that mimics the junction itself (in this case with two mirror axes). More complex molecules such as this highlight the “proximity effect” whereby the flow of heat from a given electrode to the orbitals in its vicinity is enhanced, so the molecule is generally warmer near the hot lead and cooler near the cold lead. We mention that, although more tedious, the Kekulé contributing structures\(^{38}\) can be used to understand the pattern of temperature variations in this molecule as well.

Focusing on the middle and rightmost panels of Figure 10, we find an immediate consequence of the proximity effect as \( \sigma \) is increased: nonmonotonic temperature variations due to quantum interference are washed out, and the underlying temperature gradient appears. In the rightmost panel, quantum temperature oscillations are no longer resolved, and the temperature distribution resembles a thermal dipole. Similar results were obtained for a variety of molecular junctions, suggesting that a classical temperature distribution consistent with Fourier’s law of heat transfer from an electrode E onto the molecule are shown in Figure 9. As in the case of the para and ortho BDT junctions, the rules of covalence are unambiguous and predict alternating hot and cold temperatures for the \( \pi \)-orbitals along the length of the molecule, with intermediate temperatures for the end orbitals proximal to the two electrodes, consistent with the calculated temperature distribution.

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conduction emerges when the temperature is measured with limited spatial resolution.

The transition from microscopic quantum temperature oscillations to macroscopic diffusive behavior and Fourier's law is still poorly understood. It has been argued that Fourier's law is recovered in systems with sufficient dephasing or disorder. However, we have seen that in conjugated organic molecules the quantum temperature oscillations are intimately connected to the rules of covalence describing the $\pi$-bonds of the molecule. Dephasing (or disorder) sufficient to wash out the temperature oscillations would thus necessarily sever the $\pi$-bonds and dissociate the molecule. Since the molecules studied in this article are stable at room temperature, we know that such strong dephasing cannot be present. Thus we predict that quantum temperature oscillations will be observed in molecular junctions if temperature measurements with sufficient spatial resolution are performed and that Fourier's law is a consequence of coarse-graining due to finite spatial resolution.

CONCLUSIONS

We have proposed a physically motivated and mathematically rigorous definition of an electron thermometer as an electron reservoir coupled locally to and in both thermal and electrical equilibrium with the system being measured [cf. eq 1]. This definition is valid under general nonequilibrium conditions with arbitrary thermal and/or electric bias. On the basis of this definition, we have developed a realistic model of an atomic-resolution SThM operating in the tunneling regime in ultrahigh vacuum, including the effect of thermal coupling of the probe to the ambient environment.

We used this model of an atomic-resolution SThM to investigate the nonequilibrium temperature distributions of a variety of single-molecule junctions subject to thermal gradients. Quantum oscillations of the local temperature that can be observed using an SThM with sufficiently high resolution are predicted. We show that in many cases these quantum temperature oscillations may be understood straightforwardly in terms of the rules of covalence describing bonding in $\pi$-electron systems. As such, these oscillations are predicted to be extremely robust, insensitive to dephasing or disorder that is insufficient to dissociate the molecule. Instead, we show that such quantum interference effects are washed out if the spatial resolution of the SThM is insufficient to observe them and that the temperature distribution then approaches the distribution that is expected based on Fourier's classical law of heat conduction. Reduced thermal resolution of the SThM does not wash out the temperature oscillations, but merely reduces their observed amplitude.

One may wonder whether it is meaningful to define a temperature that varies significantly from place to place at the atomic scale. Since temperature is related to mean thermal energy, does a variation of temperature on a scale comparable to the de Broglie wavelength not violate the uncertainty principle? Our answer to such questions is a pragmatic one: By definition, temperature is that which is measured by a thermometer, and the position of a thermometer can certainly be controlled with subatomic precision using standard scanning probe techniques. We should also emphasize that our proposed thermometer measures the electron temperature, which may be largely decoupled from the lattice temperature in nanoscale junctions.

Finally, let us return to the theme of the title of this article. We have shown that in a molecular junction containing a conjugated organic molecule, the rules of covalence act essentially like a Maxwell demon, in that they selectively permit electrons from the hot or cold...
reservoir to tunnel onto the probe, when it is at specific locations near the molecule, and block electrons from the other reservoir. The question might arise whether the actions of this Maxwell demon could lead to a violation of the second law of thermodynamics, as Maxwell originally hypothesized. However, in this case there is no violation of the second law, because electrons within the molecule “remember” which electrode they came from. There is no “mixing” of the hot and cold electrons in the absence of inelastic scattering, and we have argued that dephasing due to inelastic scattering is insufficient to perturb this particular embodiment of Maxwell’s demon without dissociating the molecule itself.

METHODS

Molecular Dyson Equation Many-Body Quantum Transport Theory. In the energy domain and using matrix notation, the Green’s function of a molecular junction may be expressed exactly via the molecular Dyson equation (MDE) as \[ G = G_{\text{mol}} + G_{\text{mol}} \Sigma G \] (17)

where \( G_{\text{mol}} \) is the interacting molecular Green’s function found in the limit of weak tunnel coupling to the electrodes, but including long-range Coulomb interactions between the \( \pi \)-electrons. The self-energy \( \Sigma = \Sigma_i + \Delta \Sigma_c \) where \( \Sigma_i \) is the tunneling self-energy associated with the lead-molecule bonds and \( \Delta \Sigma_c \) is the correction to the Coulomb self-energy arising from lead-molecule coherence. The molecular Dyson equation is exact: the derivation of eq 17 requires no approximations.\(^{13}\)

MDE theory describes both Coulomb blockade (particle-like) and resonant tunneling (wave-like) effects simultaneously, both of which are important in molecular junction transport experiments. Away from resonance and at room temperature \( \Delta \Sigma_c \approx 0 \), an approximation that is discussed in detail in ref 13.

The tunneling self-energy associated with a given electron can be expressed as \( \Sigma_i = \Sigma_i^{\text{C}} + \Delta \Sigma_i^{\text{C}} \), where \( \Sigma_i^{\text{C}} \) is the tunneling self-energy arising from lead-molecule coherence and \( \Delta \Sigma_i^{\text{C}} \) is the correction to the Coulomb self-energy arising from lead-molecule coherence. The molecular Dyson equation is exact: the derivation of eq 17 requires no approximations.\(^{13}\)

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As shown in the figure, the tunneling between lead \( \alpha \) and the molecule. In the wide-band limit the energy dispersion of the electrode is assumed to be slowly varying and the tunneling self-energy is given by

\[ \Sigma_i = -\frac{i}{\hbar} \sum_{\alpha} \vec{G}_0^{\alpha} \] (18)

where \( \vec{G}_0^{\alpha} \) is the tunneling-width matrix associated with lead \( \alpha \).

Aside from the self-energy, the other ingredient needed to evaluate eq 17 is the Green’s function of the isolated molecule. This is determined exactly (in the limited Hilbert space of the \( \pi \)-electrons) by first finding the few-body eigenstates \( |\psi_0\rangle \) and eigenenergies \( E_0 \) of the isolated molecule and then using these to explicitly evaluate the molecular Green’s function.\(^{13}\)

\[ G_{\text{mol}} = \sum_{i \tau} \left( \frac{|\psi_0 \rangle \langle \psi_0|}{E - (E_0 - E_i) + i\Delta} \right) \] (19)

Here \( |\psi_0 \rangle \) is the statistical occupancy of the \( \psi_0 \) eigenstate, given at equilibrium by the grand canonical ensemble (sufficient for linear response transport calculations), and

\[ C_{\text{mol,} \psi_0, \psi_0}(\nu, \nu') = \langle \psi_0 | d_{m, \nu} | \psi_0 \rangle \langle \psi_0 | d_{m, \nu'} | \psi_0 \rangle \] (20)

are many-body matrix elements. \( d_{m, \nu} \) creates an electron with spin \( \nu \) in the \( m \)th \( \pi \)-orbital of the molecule.

Equations 17–20 provide a method for obtaining the full interacting Green’s function of the molecule coupled to the electrodes, which may then be used to calculate the various physical quantities of interest. For instance, the heat and charge currents given by eq 2 involve \( G(E) \) via eqs 12 and 13.

Equilibrium Time for a Nanoscale Thermometer. The heat capacity of the probe must be sufficiently small to ensure an equilibration time that is less than any drift times in an experimental system. Using eq 3, we have

\[ \dot{I}_p^{(1)} = CV \frac{dT_p}{dt} = \vec{K}_p(T_1 - T_p) + \vec{K}_p(T_2 - T_p) \]

\[ + \vec{K}_p(T_0 - T_p) \] (21)

where \( \dot{I}_p^{(1)} \) is the heat current into the probe, and \( C \) and \( V \) are the heat capacity and volume of the metal tip of the probe, respectively. Equation 21 leads to the following first-order differential equation:

\[ \frac{dT_p}{dt} = \tau^{-1}(T_p - T_0) \] (22)

where

\[ T_p = \vec{K}_p(T_1 + \vec{K}_p T_2 + \vec{K}_p T_0) \]

\[ \vec{K}_p + \vec{K}_p + \vec{K}_p \] (23)

and the equilibration time of the temperature probe is given by

\[ \tau = \frac{CV}{\vec{K}_p + \vec{K}_p + \vec{K}_p} \] (24)

For a Pt probe tip with linear dimensions on the order of 1 \( \mu \)m, \( V = 4/3 \pi r^3 = 4.19 \times 10^{-12} \) cm\(^3\), and \( CV \leq 1.17 \times 10^{-11} \) J/K, where the specific heat \( C_{\text{N}} \) \( (133\text{ J/kgK})(0.021\text{ kg/cm}^3)\),\(^{32}\) The spatial equilibration time profiles for such a Pt probe fixed 3.5 \( \AA \)
The temperature profile of each junction is shown in Figure 5. All data here were simulated under the same conditions. In spite of the low sensitivity when $k_{p0} = 10k_0$, quantum oscillations in the temperature profile are still clearly visible in Figure 5.

Figure 12. Calculated sensitivity distributions for para-, ortho-, and meta-configured BDT junctions measured using a Pt SThM probe scanned 3.5 Å above the plane of the molecules. The temperature profile of each junction is shown in Figure 5.

above a Au–[1,4]BDT–Au and a Au–[2,7]pyrenedithiol–Au junction are shown in panels a and b of Figure 11, respectively. All calculations are performed with $k_{p0} = 0$ and are thus upper bounds on the true equilibration time given by eq 24. In both cases, the equilibration times are on the order of tens of nanoseconds when the SThM is above the molecule.

**Sensitivity.** The sensitivity profiles of para-, ortho-, and meta-configured BDT junctions measured using a Pt SThM probe scanned 3.5 Å above the plane of the molecule are shown in Figure 12. These simulations indicate that even with low sensitivity (i.e., when $k_{p0} = 10k_0$) the quantum oscillations of the temperature (cf. Figure 5) are still experimentally resolvable. With current experimental techniques $k_{p0} \approx 700k_0$, which gives a temperature range of $\sim 30 \mu K$ for the BDT junctions discussed here. In order to experimentally observe these quantum temperature oscillations, the environmental coupling to the probe will have to be decreased and/or the temperature precision increased.

**Conflict of Interest:** The authors declare no competing financial interest.

**Acknowledgment.** This material is based on work supported by the Department of Energy under Award No. DE-SC0006699.

**Supporting Information Available:** Additional simulations and analyses include here: the effect of different lead-molecule coupling and asymmetric temperature bias on the predicted quantum temperature oscillations, an electrostatic model to include the thiol linker groups and electrodes, and the details of the electronic model used in the pyrene transport calculations.

This material is available free of charge via the Internet at http://pubs.acs.org.

**REFERENCES AND NOTES**