Electronic measurements of entropy in meso- and nanoscale systems

Eugenia Pyurbeeva,¹ ², Jan A. Mol,¹ and Pascal Gehring² ³

¹School of Physics and Astronomy, Queen Mary University of London, Mile End Road, London E1 4NS, UK
²IMCN/NAPS, Université Catholique de Louvain (UCLouvain), 1348 Louvain-la-Neuve, Belgium

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Entropy is one of the most fundamental quantities in physics. For systems with few degrees of freedom, the value of entropy provides a powerful insight into its microscopic dynamics, such as the number, degeneracy and relative energies of electronic states, the value of spin, degree of localisation and entanglement, and the emergence of exotic states such as non-Abelian anyons. As the size of a system decreases, the conventional methods for measuring entropy, based on heat capacity, quickly become infeasible due to the requirement of increasingly accurate measurements of heat. Several methods to directly measure entropy of mesoscopic quantum systems have recently been developed. These methods use electronic measurements of charge, conductance and thermocurrent, rather than heat, and have been successfully applied to a wide range of systems, from quantum dots and molecules, to quantum Hall states and twisted bilayer graphene. In this Review, we provide an overview of electronic direct entropy measurement methods, discuss their theoretical background, compare their ranges of applicability and look into the directions of their future extensions and applications.

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I. INTRODUCTION

The connection between macroscopic observables and microscopic dynamics was first made by Maxwell when he attributed part of the heat capacity $C$ of a gas to the rotational degrees of freedom of its molecules. The name entropy was coined by Clausius in 1865 to describe the non-useable energy increase in a steam engine’s exhaust as a function of its temperature $T$ through the relation $dS = CdT/T$. Boltzmann and Gibbs later gave entropy its statistical basis that connects the observable averaged state functions to the microscopic dynamics of a system described by the number of microstates $\Omega$ and their probabilities, epitomised by Boltzmann’s constant $k_B$ in his definition of entropy $S = k_B \ln \Omega$. Since then, entropy measurements based on heat capacity and temperature have been used to probe the microscopic structure of bulk materials, such as the disorder in alloys, phase transitions in molecular crystals and the magnetic arrangements of spin ice.

The development of nanofabrication, in particular molecular beam epitaxy and electron beam lithography, has made it possible to confine electrons in one or more dimensions. This has enabled the measurement of heat capacity and entropy in mesoscopic systems such as two-dimensional (2D) electron gasses in GaAs quantum well structures and of fractional quantum Hall systems. These experiments present significant difficulties as the contribution to the heat capacity of the confined electronic states is generally far smaller than that of the vibrations, or phonons, in the substrate material.

To overcome this challenge, the electronic contribution to the heat capacity was increased by increasing the number of quantum wells and by exploiting the difference in thermalisation time of the electronic and phononic systems. Despite the ingenuity of these solutions, further down-scaling of entropy measurements based on heat capacity to few-electron nanodevices is practically impossible as the small numbers of electrons and electronic states involved require the measurement of increasingly small amounts of heat and heat capacities. For comparison, the maximum heat capacity of a single electronic spin is of the order of $10^{-24}$J/K, while the minimal values of heat capacity per particle experimentally measured are three orders of magnitude greater.

Yet, it is precisely in systems containing only a few particles that entropy measurements can reveal the most about...
microscopic dynamics. For example, the von Neumann entropy of the entangled state \((|00\rangle + |11\rangle)/\sqrt{2}\) is \(k_B \ln 2\), while the entropy of the product state \((|00\rangle + |01\rangle + |10\rangle + |11\rangle)/2\) is zero.\(^{12,13}\) There is therefore a strong motivation to measure the entropy of few-electron quantum systems that has led to the development of alternative ways that do not rely on detecting the prohibitively small flow of heat. Electronic entropy measurements have recently emerged to address this challenge. Unlike heat, charge is a conserved quantity, which makes it much easier to measure. Charge sensitivities down to level of \(10^{-6} \times e/\text{Hz}\) can be achieved in few-electron devices, and charge currents as small as \(10^4 \text{ e}/\text{s}\) can be detected. Both these measures, of charge state and current, can be used to determine the entropy of a system. Electronic entropy measurements are thus ideally suited to probe microscopic dynamics of few-electron quantum systems that are weakly coupled to their environment.

This Review will summarize the thermodynamic theory underpinning both charge- and current-based entropy measurements of mesoscopic quantum systems, and discuss their application to several material systems and devices, including twisted bilayer graphene,\(^{14,15}\) Kondo-systems,\(^{15,16}\) quantum Hall states, and quantum dots and quantum dot systems as well as single-molecule devices.\(^{19,20}\) In all these systems electronic entropy measurements may serve a dual purpose. On the one hand, electronic entropy measurements provide insight into the internal quantum structure of matter, and might reveal exotic quasi-particles such as Majorana fermions. On the other hand, knowledge can be gained about the operation of an entire new class of nanoscale thermodynamic systems that include single-electron heat engines that operate close to the Curzon-Alhborn limit,\(^{21}\) stochastic Maxwell demons,\(^{22,24}\) and Szilard engines\(^{25}\) and clocks.\(^{26,27}\)

In Section II of this review, we will discuss different approaches to determine entropy of bulk materials that do not rely on heat measurements. In Section III we will extend this discussion to systems with a quantised charge, and in Section IV we will discuss how these entropy measurements can be used to reveal microscopic dynamics of quantum systems under investigation. Finally, we will provide an outlook on the future of nanoscale thermodynamics and entropy measurements of quantum systems.

II. ALTERNATIVE ENTROPY MEASUREMENTS IN CONTINUOUS-CHARGE NANODEVICES

Since conventional approaches to entropy measurements are not easily applicable to mesoscopic systems, there has been great effort in developing approaches that rely on observables that are experimentally accessible in these systems, with electric measurements being the prime candidate. The thermoelectric effect, which connects heat (and therefore entropy) and charge transport has been proposed as an entropic probe for non-Abelian states.\(^{28}\) Indeed, for a free electron gas, the low-temperature Seebeck coefficient is directly proportional to the entropy per unit charge.\(^{29,30}\) While this relation holds true in a wide range of bulk material,\(^{31,32}\) it breaks down, for example, in highly anisotropic transport\(^{33}\) and should thus be used with caution in mesoscopic systems.

Going beyond the thermoelectric relation between heat and
charge transport, Maxwell relations can be used to connect the experimentally controllable magnetic field, \( B \), and temperature, \( T \), and the observable magnetisation, \( m \), electron density, \( n \), and chemical potential, \( \mu \), of a quantum Hall system to its entropy per unit area, \( \frac{\partial s}{\partial T} \)

\[
\left( \frac{\partial m}{\partial T} \right)_B = \left( \frac{\partial s}{\partial B} \right)_T
\]

This was originally proposed as an alternative to interferometry methods to detect signatures of non-Abelian interferometry. However, it can equally be applied to any electronic system with temperature and field-dependent magnetisation, such as spin-ordering transitions in low density electron-gases in Wigner crystal or Luttinger liquid states. Maxwell relations have also been used to study magic-angle twisted bi-layer graphene to reveal a Pomeranchuk-type effect (see Figure 1b).

While the thermoelectric and Maxwell relation approaches that we have described thus far are generally system-independent they rely on the implicit assumption of large particle numbers such as change in state variables such as entropy and magnetisation is linear with the change in particle number. This assumption does not necessarily hold for meso- and nanoscale systems with small numbers of particles. In the remainder of this Review we will discuss the conceptual and experimental differences between entropy measurements in what we term continuous-charge devices and quantised-charge devices.

III. QUANTISED-CHARGE NANODEVICES

A. The effects of charge quantisation

We define quantised-charge devices as those meso- and nanoscale systems for which partial derivatives with respect to particle number \( N \) are undefined. It is important to note that these devices do not necessarily contain a smaller total number of particles than a continuous-charge device, but rather that they have a non-linear energy-particle relation and typically contain a smaller number of available particle number states. The most common example of quantised-charge devices are meso- or nanoscale systems that exhibit Coulomb blockade, meaning the electrostatic Coulomb repulsion is the dominant energy scale and only a small number of charge states (values of particle number in the system) are energetically accessible. Coulomb blockade is regularly observed in devices based on lithographically-defined quantum dots (see Figure 1b), and in single-atom and single-molecule devices (see Figure 1b).

The change of the electrostatic energy depends on the particle number itself as

\[
E_{el}(N+1) - E_{el}(N) = 2e^2/C \left( N + \frac{1}{2} - N_0 \right)
\]

where \( E_{el} \) is the electrostatic energy of the system, \( C \) is its capacitance, and \( N_0 \) is the background charge. Therefore, a partial derivative of energy with respect to particle number cannot be defined for systems in which the electrostatic energy dominates, even though they may contain a large number of particles, \( N_0 \). Moreover, in Coulomb-blocked devices where only two charge states are energetically accessible and \( \Delta N=1 \), no linearisation of any state variable can be justified, since

\[
\left( \frac{\partial X}{\partial N} \right)_Y \neq \frac{X(N+1) - X(N)}{\Delta N} = X(N+1) - X(N).
\]

Additionally, the partial derivative at constant \( Y \) cannot be defined, as each charge state is associated with its own value of \( Y \). This means that the approach developed for continuous-charge devices cannot be applied directly to quantised-charge devices.

B. Thermodynamic parameters of a quantised-charge system

One of the main strengths of thermodynamics is system-independence. A thermodynamic treatment of quantised-charge devices, analogous to the Maxwell relations for continuous-charge devices, allows for the development of entropy measurement methods that describe the general quantum dynamics of such systems. To do this, we will first specify the parameters (state variables) used in the thermodynamic description of small quantised-charge systems, namely the temperature \( T \), chemical potential \( \mu \), particle number \( N \), and entropy \( S \).

Temperature. While a quantised-charge system, or its electronic state dynamics may or may not be sufficiently large to have its own definable temperature, the Maxwell equation approach taken in section II requires equilibrium conditions. Following this, we may take the temperature of the nanoscale system to be equal to the well-defined temperature of the bath with which it exchanges electrons. In the case of more than one bath being present, equilibrium is only possible when the temperature differences between the baths are infinitesimally small.

Chemical potential. In quantum dot literature, the energy difference between the charge states \( \epsilon = U(N+1) - U(N) \) is often referred to as the chemical potential \( \mu \). However, this does not agree with the canonical definition of the chemical potential \( \mu = (\partial U/\partial N)_S \) due to reasons outlined after equation 2. Instead, for quantised-charge systems, one should take the approach similar to that of temperature if a system is in equilibrium with a bath regarding particle exchange, its chemical potential is equal to that of the bath. And if several baths are present, for quasi-equilibrium conditions the difference in chemical potentials must be infinitesimally small. For all realistic temperatures at which nanoelectronic measurements are performed, the electron gas that forms the bath is highly degenerate and the chemical potential of the bath and the system are to a high degree of accuracy equal to the Fermi energy, \( \mu = E_F \).

Particle number. When we consider a quantised-charge device that exhibits Coulomb blockade, the particle number...
FIG. 2. Entropic effects in charge state and charge transport measurements in quantised-state nanodevices. a) A schematic of a charge state measurement setup. An energy level coupled to a thermal bath, with the charge state of the level independently determined. b) The mean excess population \( n \) of the energy level in the case of the non-degenerate and two-fold degenerate energy level (\( \Delta S = 0 \) or \( \Delta S = \pm \ln 2 \)). c) A model of experimental time-resolved measurement of the charge state of the device. Information of entropy (or degeneracy) can be extracted from the proportion of time the device spends in each of the charge states. d) A model of the experiment performed in [17]. e) A model of the experiment performed in [17]. f) A model of the experiment performed in [17].

- Charge-state effects
- Transport effects

C. Maxwell relations in quantised-charge systems

Taking the considerations for the treatment of independent thermodynamic parameters outlined in Section III B, the standard Maxwell relation should be interpreted as

\[
\left( \frac{\partial \mu}{\partial T} \right)_N = - \left( \frac{\partial S}{\partial N} \right)_T
\]

where \( \mu \) is the chemical potential of the bath, \( \tilde{N} \) is the mean time-averaged population of the system and \( \tilde{S} \) is the Gibbs entropy incorporating both charge state uncertainty and the entropy of each charge state. However, since it is the difference between the single-particle energy of the system and the chemical potential of the bath that is proportional to the externally controlled gate voltage applied to a quantised-charge device, \( \varepsilon - \mu \approx V_G \), it is more useful to derive a Maxwell relation for this difference rather than for the chemical potential.

Such a relation, which we name the Microscopic Maxwell Relation, can be derived by considering the mean free energy...
of the system, $\tilde{F} = U(N) + \epsilon n - T \tilde{S}$, and the general relation relation for the chemical potential $\mu = (\partial \tilde{F} / \partial \tilde{N})_T$, which yields

$$\varepsilon - \mu = T \left( \frac{\partial S}{\partial N} \right)_T. \quad (8)$$

Since $N$ is constant we can replace all derivatives with respect to $\tilde{N}$ with derivatives with respect to $n$ and arrive at what we call the \textit{Microscopic Maxwell Relation}:\cite{49}

$$\varepsilon - \mu = k_B \ln \frac{1 - n}{n} + \Delta S. \quad (9)$$

In a different approach, which we name the \textit{Integral Maxwell Relation} the Maxwell relation (equation 7) can be reformulated in terms of the time-averaged particle number $\bar{N}$ and the chemical potential of the bath as: \cite{50,51}

$$\Delta S_{\mu_1 \rightarrow \mu_2} = \int_{\mu_1}^{\mu_2} d\bar{N} d\mu. \quad (10)$$

The benefit of Equation 10 is that it is completely equivalent to the Maxwell relation and therefore holds true for all systems. It has to be noted, however, that in it $\Delta S_{\mu_1 \rightarrow \mu_2}$ is the total entropy difference, with no distinction between the entropy due to the charge state uncertainty and the entropy of the pure charge states. Thus, in order to find $\Delta S$ between the charge states, one has to shift $\mu$ (or, equivalently $\varepsilon$) from the point of a pure $N$ charge state to that a pure $N + 1$ charge state: in the approximation of only two states being available, from $-\infty$ to $\infty$, but in reality between the two consecutive Coulomb-blocked regions.

### D. Quantised-charge entropy measurement methods

Entropy measurement protocols can be divided into two groups – those based on charge state measurement and those based on charge transport. 

\textbf{Charge-state based measurements} The first demonstration of an electronic entropy measurement method was based on a charge-state technique that employed the thermal shift of the charge degeneracy ($n = 1/2$) point (see Fig. 2b) as a measure for entropy difference between the charge states. A quantum point contact (QPC) was located close to a quantum dot in a GaAs lithographically-defined device and used as a mean charge sensor (Fig. 1b). The dependence of mean charge of the dot on the transport energy level was measured at two temperatures, and the entropy difference was found by fitting the asymmetry of the difference curve (Fig. 2i).

The energy $\varepsilon$ at which the probabilities of both charge states are equal, denoted $\varepsilon_{1/2}$, is given by Equation 9 with $n = 1/2$

$$\varepsilon_{1/2} - \mu = T \Delta S \quad (11)$$

which gives the thermal shift

$$\frac{\partial \varepsilon_{1/2}}{\partial T} = \Delta S. \quad (12)$$

Building on the first charge-state based entropy measurement methods,\cite{52,53} the applicability of the entropy measurement method for the detection of Majorana zero modes has been theoretically shown\cite{54} (see Section 4.A) using the integral Maxwell relation formulation. Further experimental developments concerned the design of a bespoke device and an optimised measurement protocol improving thermal equilibration in the system,\cite{55}, and the measurement of the entropy as a function of coupling strength (lifetime of a charge state), that could be controlled by gates forming the quantum dot.\cite{56}

\textbf{Charge transport based measurements} The first charge transport entropy measurement protocol that was experimentally demonstrated used simultaneous measurements of conductance and thermocurrent and inferred the entropy from fitting the thermocurrent to the following equation:\cite{57}

$$L(\varepsilon, T) = C(T) L_N(\mu + \Delta(T), T) + G(\mu, T) \frac{\Delta(T)}{T}, \quad (13)$$

where $L$ is the thermolectric conductance $L = \partial I / \partial \Delta T$ of the device, $L_N$ is the thermolectric conductance of the non-interacting (non-degenerate) level, which is symmetric in $\varepsilon, G$ is the electrical conductance and $\Delta(T)$ is a function of entropy such that $\partial \Delta(T) / \partial T = \Delta S / 2$.

The first transport-based entropy measurement approach was subsequently generalised using the observation that Equation 9 can be written to give an expression of the excess number of electrons as a shifted Fermi distribution, $n = f(\varepsilon - T \Delta S)$ which yields the following equations for the conductance

$$G \propto \frac{1}{T} \left[ 1 - f(\varepsilon) \right] f(\varepsilon - T \Delta S), \quad (14)$$

and thermoelectric conductance

$$L \propto \frac{\varepsilon}{T^2} \left[ 1 - f(\varepsilon) \right] f(\varepsilon - T \Delta S). \quad (15)$$

From this it follows that the energy for which the conductance is maximum, $\varepsilon_G$, is given by

$$\varepsilon_G - \mu = \frac{T \Delta S}{2}, \quad (16)$$

and that therefore the thermal shift of the $G(\varepsilon)$ peak position (see Fig. 2e) is

$$\frac{\partial \varepsilon_G}{\partial T} = \frac{\Delta S}{2}. \quad (17)$$

Moreover, the entropy difference between two charge states can be directly measured from the asymmetry of the thermolectric conductance $L(\varepsilon)$ (see Fig. 2h).

### E. Limitations of entropy measurement methods

Both realisations of the Maxwell relation in microscopic systems (equations 9, 10) follow from the standard thermodynamic Maxwell relation and therefore apply to a wide range
of systems. However, some physical properties manifesting in nanodevices are usually not considered in standard "macroscopic" thermodynamics. The two most obvious ones are vibrational effects and lifetime broadening.

It has been experimentally shown that mechanical degrees of freedom significantly affect charge transport in weakly coupled molecular devices.\(^{53,54}\) This was described by introducing a new energy parameter – the reconfiguration energy \(\lambda\) – which quantifies the energy that is lost to the phonon bath due to the relaxation preformed by the molecule after an additional electron is added.\(^{55}\) This energy can be associated with an entropy change \(\Delta S_{ph} = \lambda / T_{ph}\) of the phonon bath, where \(T_{ph}\) is its temperature. However, this loss of energy to the bath means that each of the charge states can no longer be attributed to a particular entropy value. Therefore, systems with strong coupling between electronic and mechanical degrees of freedom are not described by the existing theory. At the same time, they offer a potential avenue of further work into electronic characterisation of mechanical states in systems with strong electronic-mechanical coupling.

In the rate equation approach lifetime broadening is represented by a Lorentzian-shaped peak replacing the \(\delta\)-function for the energy of the transport level.\(^{40}\) From the quantum-mechanical point of view, a finite electron lifetime in the charge states means that the number and energy operators, \(\hat{N}\) and \(\hat{\varepsilon}\), no longer commute. This invalidates any equation containing \(\varepsilon\) and \(n\) simultaneously, such as equation \(^9\). However the integral form of the Maxwell relation (equation \(^{10}\)) appears to hold, as it only uses the chemical potential of the bath, and the dependence of entropy on coupling strength (lifetime) has been experimentally measured.\(^{49}\) A fundamental explanation of the measured entropy remains an interesting theoretical problem.

Charge-transport based entropy measurement methods possess more limitations than the charge-state ones. Unlike mean charge, any transport property – conductance, thermocurrent, power factor, etc. – is fundamentally a non-equilibrium quantity and therefore is not necessarily linked to the state function entropy. Furthermore, the derivation of all existing charge transport entropy measurement methods assume small level splitting – a requirement that all energy states of the system observe the same electron population. This requirement was well-formulated in the SI to \(^{18}\): "one of the levels dominates the transport, or the levels are degenerate, or at high temperatures \((T \gg \delta \varepsilon)\) or at low temperatures \((T \ll \delta \varepsilon)\)”. At the same time, a strength of transport-based entropy measurement methods is that they can be performed on devices that are otherwise widely studied, usually for thermoelectric research. In some cases,\(^{56,57}\) they can even be used as a post-factum analysis of existing experimental data.
Section 2

A. Detection of non-Abelian anyons

One of the motivating factors behind the development of electronic entropy measurement methods is to detect non-Abelian anyons, or Majorana modes. Theory predicts that Majorana modes have the potential to speed up and increase the precision in quantum computing. Majorana qubits support non-Abelian statistics, braiding and fault tolerant operation.

Several physical systems have been predicted to host Majorana modes, but their detection and control is very challenging and has not yet been achieved in a way that could be taken as proof beyond reasonable doubt. Most attempts focus on electrical fingerprinting, but a key drawback of this approach is that the minute conductance signatures of Majorana modes could be easily misinterpreted or confused with those originating from other mechanisms, especially in disordered samples.

However, it has been predicted that nonlocal Majorana zero mode (MZM) states can be detected through their entropic signature, while a Majorana qubit — a nonlocal two-level system formed by two MZMs — has a trivial entropy of $k_B \ln 2$, a single MZM should possess an universal fractional entropy of $\frac{1}{2} k_B \ln 2$ which is difficult to explain through different means.

The main challenge is creating a system in which the entropy of a single quasiparticle can be measured in a charge measurement setup. The finite coupling between two MZMs forming the Majorana qubit can be reduced either by increasing their spatial separation or by controlling the tunneling phases of the MZMs via, for example, local gates controlling the tunneling barriers between topological superconductors and quantum dots. Alternatively, experiments can be simplified by increasing the temperature, which diminishes the dependence of entropy on the MZM tunneling phases, and by involving multiple MZMs. In the latter case the sensitivity adjustment of the tunneling phases becomes obsolete and an entropy of $\frac{1}{2} k_B \ln 2$, where $n$ is the number of MZMs, is expected.

A single spin-1/2 impurity that is anti-ferromagnetically coupled to a single conduction electron channel gives rise to single channel Kondo effect. Such Kondo effect is universal and its universality has recently been verified by thermocurrent spectroscopy. At high temperatures the impurity is free and acts as an unpaired spin with entropy $k_B \ln 2$, while at low temperatures it is screened by conduction electrons (a "Kondo cloud"), forming a many-body-singlet with zero residual entropy. However, in the case of multiple conduction electron channels the impurity can be "overscreened" and a finite (non-zero) residual entropy is expected. It has been predicted that such systems can host Majorana fermions with a residual impurity entropy of $k_B \ln \sqrt{2}$ when two channels are present, or, in the case of more — Fibonacci anyons with $k_B \ln \phi$, where $\phi = \frac{1}{2}(1 + \sqrt{5})$ is the golden ratio. A promising experimental realisation for the multi-channel Kondo model are charge Kondo quantum dot devices, which hold the potential for detection of non-Abelian anyons through entropy measurements.

B. Twisted bilayer graphene

Recently electronic entropy measurements have been conducted in twisted bilayer graphene. This is a continuous-charged system, so the extension of theory allowing for charge quantisation was not required, and instead the Maxwell relation approach outlined in Section II was used.

Typically, thermodynamic states with high entropy are more stable at higher temperatures than states with low entropy. The two recent entropy measurements in twisted bilayer graphene revealed an exotic phenomenon which seemingly violates this intuitive picture.

Both studies measured the temperature-dependent change of the electrochemical potential $\mu$ of one-quarter-filled twisted bilayer graphene, either directly or by integrating the inverse local electronic compressibility, which was measured by a nanotube-based scanning single electron transistor (see Figure 1a). The entropy of the system could then be determined by using a Maxwell relation (see Equation 2).

It was found that the entropy per electron of the high-temperature, electrically insulating phase is greater than that of the low-temperature, metallic phase by an amount corresponding to a single free spin. The suggested explanation for this is that the high-temperature insulating phase adopts a ferromagnetic order, in which the iso-spins (a combination of valley and spin degree of freedom) are globally aligned in one preferred direction, but the constraint on their alignment is weak. In the metallic phase, on the other hand, the constraint on iso-spin alignment is high ensuring a non-magnetic state with an equal number of iso-spins with opposite orientations. Consequently the stability of the ferromagnetic insulating state is favoured at elevated temperatures due to its slightly higher entropy. A similar effect is known as the Pomeranchuk effect in He$_3$, which solidifies when the temperature is increased.

C. Single electron transistors and single molecule devices

The recent resurgence in interest towards electronic entropy measurement methods is focused on single electron transistors (SETs) — devices in which electrical transport is dictated by Coulomb repulsion. SETs have been realised in a wide range of systems: from electron gases, semiconductors, to single molecule junctions. The theoretical description of quantised-charge entropy measurements in Section II is system-independent and only relies on few charge-states being energetically available.

Entropy measurements based on charge sensing were demonstrated as proof of concept in [17] (see Figure 1b). To this end, the entropy differences were measured for the $N = 0 \leftrightarrow N = 1$ and $N = 1 \leftrightarrow N = 2$ charge state transitions. A precise value of $k_B \ln 2$ of a single spin 1/2 was found in...
the first transition (Figure 3a), while a singlet to triplet transition was observed in the \( N = 2 \) charge states at high magnetic fields (Figure 3b). Such precise entropy measurements can be used for probing more exotic systems like those with non-Abelian statistics (see Section IIIA "Detection of non-Abelian anyons").

Molecular electronics, the concept of using single molecules as building blocks of nanodevices, gained enormous theoretical and experimental interest over the last decades. Molecules are fundamentally perfectly reproducible and their length scales of 1-3 nm offer a platform for downscaling and surpassing the limitations of conventional silicon-based technologies \(^{22}\) by harnessing the achievements of chemical synthesis. \(^{23,24}\) Thermoelectric research of molecular devices has received continuously growing attention in recent years for potential applications in energy conversion and solid-state cooling. \(^{27,81,85}\)

Degeneracy of energy levels in single-molecule devices is of interest, as it has recently been suggested that molecular systems with highly degenerate ground states can lead to exceptionally high thermoelectric power factors. \(^{55}\) A conductance-based entropy measurement in a Gd-terpyridine complex (Figure 1c), which followed the method depicted in Figure 2g, indeed shows an enhancement of the power factor of the thermoelectric junction by spin entropy, originating from energy level degeneracy. \(^{29}\)

Beyond finding strategies to enhance the thermoelectric efficiency, thermoelectric experiments on single-molecule junctions can furthermore serve as a novel kind of spectroscopy, which allows to deduce the energy level structure of a molecule from its thermoelectric properties. As proof of concept, this was demonstrated on a radical molecule \(^{52}\) (see Fig. 3c-d) revealing the presence of a triplet state in the reduced state of the molecule, as well as extracting the energy of the singlet-triplet transition.

V. OUTLOOK AND CONCLUSIONS

This review has examined the latest chapter in the long history of entropy measurements as a macroscopic probe for microscopic dynamics. Unlike conventional entropy measurements based on heat, these latest measurements probe entropy directly from electronic measurements in nanodevices. This idea was first proposed in the early 2000s and has gained attention in the past few years.

Currently, the field is in transition from proof-of-concept experiments, measuring the entropy of a simple degenerate level \(^{17,18}\) and conceptual theoretical work \(^{50}\) to practical applications, which involved the demonstration of a Pomeranchuk-type effect in twisted bilayer graphene \(^{14,15}\) and the measurement of the singlet-triplet transition energy in a single-molecule device. In the area of detection of non-Abelian anyons the theoretical background is in place and current work is focused on improving experimental devices for greater experimental accuracy. \(^{51}\)

As electronic entropy measurements complete the transition to yet another tool in the experimentalist’s toolbox, they will have two distinct applications. First, entropic signatures can be used for detection, as it is proposed for non-Abelian anyons. Secondly, the value of entropy can allow to determine microscopic dynamics of a system with no a-priori knowledge, as it was demonstrated in twisted bilayer graphene \(^{14,15}\) and in a single-molecule device. \(^{52}\)

In this review we have attempted to develop a taxonomy for existing electronic measurement techniques, and to reveal their underlying thermodynamic principles, as well as their limitations.

The consideration of limitations itself opens up new questions and areas of research. Examples of these include studying mechanical degrees of freedom in systems with strong electron-vibrational coupling and devices in the rarely-considered intermediate case between the Landauer regime and weakly-coupled sequential tunnelling, in which lifetime in the device is small and has a significant contribution to entropy. \(^{59}\)

Finally, the ability to measure thermodynamic parameters, primarily entropy, in nanodevices opens them up as an experimental platform for studying stochastic, and especially quantum thermodynamics. This is in contrast with the usual bottom-up experimental approach to the field \(^{78-80}\), but has the benefit of years of technological advancement of nanodevices for practical applications, as well as ease of experimentation. This approach would require additional theoretical work, as the term “open quantum systems” usually implies systems open to energy, but not particle exchange. However the experimental accessibility of electrical nanodevices which include both justifies this effort.

In summary, to date, the field has focused on developing novel measurement techniques and conceptual demonstration of entropy measurements in a range of systems. Moving forwards, the next stage will be to apply these techniques in a systematic way to uncover microscopic dynamics of quantum correlated systems, potentially discover new and exotic quasiparticles in condensed matter systems, as well as expand the theoretical background for more fundamental applications.

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