Employing different statistical ensembles may lead to qualitatively different results concerning averages of physical observables on the mesoscopic scale. Here we discuss differences between the canonical and the grandcanonical ensembles due to both quenched disorder and thermodynamical effects. We show how these differences are related to spectral correlations of the system at hand, and evaluate the conditions (temperature, system’s size) when the thermodynamic limit is achieved. We demonstrate our approach by evaluating the heat capacity, persistent currents and the occupation probability of single electron states, employing a systematic diagrammatic approach.

I. INTRODUCTION

Standard textbooks on equilibrium statistical mechanics often assert that the various statistical ensembles in standard use (e.g., the canonical ensemble (CE) and the grandcanonical ensemble (GCE) are equivalent. Landau and Lifshits [1] assert hat “… all three distributions, the microcanonical and the two forms of the Gibbs distribution, are in principle suitable for determining the thermodynamic properties of the body. The only difference from this point of view lies in the degree of mathematical convenience”. Huang [2] claims that “… the grand canonical ensemble is trivially equivalent to the canonical ensemble for N particles”, and there are many more examples. These assertions should be understood as referring to average thermodynamic quantities (as distinct from fluctuations; it is evident that by the very nature of the respective ensembles, fluctuations in the number of particles, for example, are very different between the CE nd the GCE). Moreover, it is assumed that the body under consideration is macroscopic (i.e., the “thermodynamical limit” has been taken). In this limit the relative fluctuations tend to zero.

It is important to stress, though, that thermodynamic (or statistical-mechanical) quantities may be perfectly defined even for a system with few degrees of freedom – provided they are in equilibrium with an infinite reservoir (heat bath, particle reservoir, etc.). A well-known example is the Fermi-Dirac distribution function which is obtained by considering a single-level system coupled (weakly) to an electron bath at temperature T and chemical potential μ. In the limit of small systems fluctuations are large (relative to mean values). As we have stressed above, their nature is very different between the different ensembles. More interestingly, average thermodynamic quantities too may be different between the CE and the GCE. Most strikingly, qualitative differences between the two ensembles may arise when quantum coherence comes into play, on mesoscopic scales and downwards. Novel effects may appear, which are quite remote from our common wisdom and everyday intuition as applied to macroscopic systems in the thermodynamic limit. The thermodynamic limit is attained as the system’s size tends to infinity and/or when the temperature is made sufficiently high.

It is evidently interesting to identify the scale of temperature (in conjunction with the system’s size) at which the non-trivial differences (i.e., differences in mean values, possibly qualitative) between the CE and the GCE are suppressed. Furthermore, we shall note that on finite length or temperature scales there are certain differences between thermodynamic relations and statistical-mechanical ones (therefore these two different frameworks may lead to different predictions, although, as was noted above, both statistical mechanics and thermodynamics are well-
defined even in the context of finite systems. Consequently there are characteristic temperature or length scales which mark the suppression of the differences between statistical mechanics and thermodynamics, and the crossover to the “thermodynamic limit”.

It should be stressed that in most practical instances the fabrication of samples is not a perfectly reproducible process. Commonly there are sample-to-sample variations in sample size and shape, in the mesoscopic impurity configuration and the location defects (we shall refer to all these factors as “disorder”). Evidently it is possible to ask questions pertaining to sample specific observables, and to evaluate the magnitude of sample-to-sample fluctuations in these observables. But it is also of interest to consider ensemble averaged quantities, where averaging over disorder is included (the concept of ensemble will be elucidated below). Such ensemble averaged quantities will be at the focus of the present study.

The purpose of this paper is twofold. We shall first review and expand on the differences between the CE and the GCE (in the context of ensemble averaged quantities) both due to quenched disorder and to thermodynamic fluctuations. The latter is manifest only at finite temperatures. This part includes careful examination of the notion of these ensembles in conjunction with the proper averaging procedures. Secondly, we shall address certain questions central to our understanding of statistical mechanics and thermodynamics on the mesoscopic scale. Thes questions include the following points: (1) We shall identify the (length scale dependent) temperature over which differences between the two ensembles are suppressed. (2) We shall relate this to the temperature (or length) scale over which differences between statistical mechanics and thermodynamics are suppressed. We shall thus identify the scales at which the thermodynamic limit is approached. (3) We shall relate the above to energy scales characterizing correlations of the underlying energy spectrum. These concepts will be illustrated below.

The scope of the questions addressed here is quite general and includes generic many body systems. Our quantitative discussion, though, will be carried out for systems of noninteracting electrons.

The outline of this paper is as follows.

In Section 2 we discuss various definitions of “canonical” and “grandcanonical”. We distinguish between fluctuations in the number of particles (electrons), $\delta N$, which are due to thermodynamical effects, as opposed to quenched disorder induced $\delta N$. We also discuss the difference between canonical (or grandcanonical) constraints, defined with respect to the way the system is prepared (at equilibrium), and such constrains as defined when the system under consideration is subject to a dynamical perturbation. We next explain how to express ensemble averaged canonical quantities in terms of ensemble averaged grandcanonical quantities and fluctuations thereof. This is done at zero temperature and is presented as an expansion to an arbitrary order in a small parameter.

Section 3 contains a discussion of the differences between the CE and the GCE at finite temperature. This is related to differences between thermodynamics and statistical mechanics on the mesoscopic scale. Exact thermodynamic identities should be corrected when finite systems (at finite temperatures) are considered within the framework of statistical mechanics. This further modifies the relations between the CE and the GCE found above at T=0 alluded to above. We find how these differences between thermodynamic identities and statistical mechanical relations depend on temperature (and system’s size) and evaluate the scale over which crossover to the “thermodynamic limit” takes place. It turns out that this scale (say, in temperature) is usually much larger than what one might normally guess.
(namely, that it is of the order of the level spacing). We demonstrate our approach by evaluating the manner in which three different physical observables depend on the type of the ensemble employed; these observables are the heat capacity, the persistent current and the single level occupation probability. Differences between grandcanonically and canonically averaged quantities (e.g., the Fermi-Dirac distribution function and its canonical counterpart) are due to both quenched disorder and thermodynamic fluctuations.

II. STATISTICAL ENSEMBLES AND QUENCHED DISORDER: T=0

2a What Do We Mean by “Canonical” and “Grandcanonical” Conditions: Particle Fluctuations and Various Averaging Procedures

The notion of ensemble averaging is in the very heart of statistical mechanics. Rather than considering a particular time evolution of a specific system with given initial conditions, we consider an ensemble of systems (or a set of initial conditions) and average over them with appropriate weights, stipulating that in any given set of experiments (or in an experiment that lasts a finite period of time) the experimental conditions are generally not reproducible to the last minute detail, but rather random sampling of the systems which form the ensemble takes place.

The concept of a grandcanonical ensemble (as opposed to a canonical ensemble) invokes the notion of fluctuations in the number of particles, \( \delta N \). (In our case we shall refer to fluctuations in the number of electrons in the system). We now describe four different thought experiments which help us to eliminate some confusion that arises in the literature regarding what really is meant by CE or GCE.

Experiment 1: We consider a system (in our context a mesoscopic conductor with disorder) coupled weakly to an external reservoir at temperature \( T \) and a chemical potential \( \mu \) (Fig. 1a). The system will reach equilibrium with the external reservoir (if the coupling is weak the equilibration time may be long, but we are not interested here in transients). Even when equilibrium is attained the number of electrons in the system may still fluctuate in time; at finite temperature the system may exchange electrons with the reservoir. Denoting the number of electrons at times \( t_1, t_2, \ldots, t_n \) by \( N_1, N_2, \ldots, N_n \) we obtain a fluctuating sequence of numbers, whose variance is \( \delta N^{(1)} \).

Experiment 2: We consider identical microscopic replica of the same mesoscopic systems, all weakly coupled to the same external reservoir (Fig. 1b). Measuring the number of electrons in each system (at equilibrium) at a given arbitrary time we obtain a fluctuating sequence \( N_1, N_2, \ldots, N_n \) whose variance is denoted as \( \delta N^{(2)} \).

By the ergodic hypothesis \( \delta N^{(1)} = \delta N^{(2)} \). Moreover, they both tend to zero at \( T \to 0 \). This reflects the fact that the origin of these fluctuations is dynamical: the Hamiltonian of the system contains a (small) coupling term to the reservoir. The number of electrons in the system is, therefore, not a conserved quantity. Evidently in the limit of \( T \to 0 \), when the level broadening in the system due to the coupling term is smaller than the level spacing, and if \( \mu \) is chosen to fall within the “gap” between two consecutive levels, the exchange of electrons with the reservoir is suppressed.

Experiment 3: We now consider an ensemble of mesoscopic conductors which are macroscopically similar (they are made of the same material, are characterized by the same volume and impurity concentration, etc.) but are microscopically distinct (small variations in shape; different impurity configurations (Fig. 1c)). All these systems are
weakly coupled, and equilibrated, with the same external reservoir. As a result, to each member of this ensemble corresponds a different spectrum (cf. Fig. 2a). Thus, even at T=0 (and with every member possessing the same value of chemical potential) different members of the ensemble will have different numbers of electrons. This defines $\delta N^{(3)}$ which does not vanish even in the $T \to 0$ limit. The origin of this $\delta N^{(3)}$ is quenched disorder.

**Experiment 4:** We may consider a single member of the ensemble at equilibrium, as function of an externally controlled parameter (magnetic field, Aharonov-Bohm (AB) flux, electric field, external pressure, etc.) (Fig. 1d). We shall denote this external parameter by $\Phi$. Generally the spectrum of the system depends on $\Phi$. A generic situation is depicted in Fig. 2b. The number of particles (occupied levels) at equilibrium varies with $\Phi$ (e.g., at T=0 $N(\Phi_1 = 2$, $N(\Phi_2 = 3$, cf. Fig. 2b), which defines $\delta N^{(4)}$. Again, this quantity does not vanish even in the limit $T \to 0$. The order of magnitude of $\delta N^{(3)}$ and $\delta N^{(4)}$ may be very different. For diffusive systems with $\Phi$ representing an AB flux it has been found by Altshuler and Shklovskii [4,5] that for a two-dimensional system ($d=2$) and hard core scatterers $\delta N^{(3)} \sim \hbar/E_c \tau$ (for $(\frac{\ell}{\ell})^2 \gg 1$) where $\tau$ is the elastic mean free time and $E_c = \frac{\hbar D}{L^2}$ is the Thouless energy ($L$ is the system’s linear size; $\ell$ is the elastic mean file path, $D$ is the diffusivity). By contrast [6] $\delta N^{(4)} \sim 1$.

In the first part of this paper we shall set the temperature to be zero. We shall thus suppress any dynamic fluctuations in $\delta N$, and the distinction between the GCE and the CE will be based on whether or not there are fluctuations in the number of particles due to quenched disorder. (Only at a later stage shall we also consider finite temperatures). Thus, in the present context we shall employ the term CE to refer to a set of finite systems whose (sample specific) number of electrons $N^i$ ($i$ is used here as an index for the ensemble member) is selected independently of the disorder dependent energy spectrum, and is specifically $\Phi$ independent. Similarly, a GCE implies that the sample specific chemical potential, $\mu^i$, is selected independently of the disorder energy spectrum, and is specifically $\Phi$ independent. Throughout most of this paper we shall consider systems of noninteracting electrons, although some of the notions here may be generalized to include systems of interacting particles.

It is possible to refer to a strong CE where $N^i = N$ for all $i$, and similarly to a strong GCE where $\mu^i = \mu$ for all $i$ (these were implicitly the conditions in Refs. 6-10 and Ref. 4, respectively). Alternatively, averaging within the CE (GCE) may be realized by randomly selecting values for $N^i(\mu^i)$ out of a broad and smooth distributions. We shall refer to these as weak CE (GCE) respectively. Below we shall argue that in many generic situations strong and weak averaging scenarios, as defined above, are equivalent, and will exploit this equivalence to our advantage. Figs. 3a,b depict schematically typical strong CE and strong GCE scenarios respectively. In Fig. 3a the probability that $\mu$ falls in a given interval between two levels is proportional to the distance (“gap”) between these two levels. The effective (sample specific) chemical potential in the CE ($T \gg \Delta$) is located half way between the last occupied ($N^i\Delta$) level and the first vacant ($N + 1\Delta$) level [11], Fig. 3b, regardless of the size of the interlevel gap. Thus, compared with the GCE, there is an enhanced probability to find narrow gaps in the vicinity of the effective chemical potential in the CE. The implications of this observation will become apparent below.

The distinction among various types of ensembles may be carried further if we note that the nature of the ensemble depends conceptually on both the way it is prepared (brought into equilibrium), and the conditions under which the system is allowed to respond to an external bias. To be specific, let us consider an ensemble of multiply connected Aharonov-Bohm rings, subjected to magnetic flux, $\Phi$, threading each of them. At the preparation stage (which takes
place at flux $\Phi$), the rings may be brought into equilibrium either subject to canonical conditions ($\{N^i\}$ are chosen to be random independent parameters, i.e., the number of electrons at each ring is selected independently of the ring’s specific impurity configuration), or in accordance with grandcanonical conditions ($\{\mu^i\}$ are chosen independently of the impurity configuration). Subsequently, one performs measurements (e.g. of the ring’s magnetic moments) at the flux $\Phi$. Then, too, as $\Phi$ is varied (to obtain the response of the system), either canonical (number of electrons is kept unchanged) or grandcanonical (value of chemical potential is set fixed) conditions may be adopted. According to this classification, where a distinction is made between the preparation and the measurement stages, the CE is now denoted as canonical-canonical (C-C) and the GCE as GC-GC. We may also consider an intermediate, “hybrid” type of ensemble, GC-C. This “hybrid” procedure implies that the number of particles remains unchanged during the time $\Phi$ is varied. This situation is achieved either when the system is decoupled from the reservoir before $\Phi$ is varied, or if the coupling strength, $\gamma$, (affecting the inelastic broadening of the levels) satisfies $\gamma < \omega_{bias}^{-1}$ where $\omega_{bias}$ is the characteristic time scale for time modulations of the external bias. For $\gamma > \omega_{bias}$ the response to the external bias may be referred to as grandcanonical. We note that as long as we allow for (weak) coupling to the particle bath (which is necessary at the stage the system is prepared grandcanonically) and do not turn it off completely, the GC-C procedure is not an adiabatic one: when the rate of change of $\Phi$ is slower than any other time scale in the system the procedure converges toward a GC-GC procedure.

Following the above discussion and referring to the nature of both the preparation and measurement stages, we may consider GC-GC, C-C or GC-C procedures. At least in principle, one may realize these various ensembles experimentally [13,14]. The fourth combination, C-GC, is not physically relevant. Evidently the procedure we take at any given stage needs not be purely canonical or grandcanonical. For example, we may select the number of electrons within each ring to be only slightly correlated with the ring’s disorder configuration. Thus there is a whole continuum of statistical procedures.

2b Relations Among Various Statistical Ensembles: T=0

Returning now to the two principle ensembles (CE and GCE, or, employing our alternative notation, C-C and GC-GC), it is desirable to find a relation between averages taken within the two ensembles respectively. From the calculational point of view, the GCE is more amenable to analytical studies (employing, e.g., disorder Green function techniques, random matrix theory (RMT), or supersymmetric (SUSY) calculations).

To derive a general relation between GCE and CE averages we consider a strong GCE situation. The (thermodynamic average) number of electrons in the $i^{th}$ member of the ensemble is given by

$$N^i(\Phi, \mu) = \int d\epsilon \nu^i(\epsilon, \Phi) f(\epsilon - \mu), \quad (1)$$

where $\mu = \text{const.}$ and $\nu^i(\epsilon, \Phi)$ is a sample and flux dependent density of states (to be more concrete we presently assign to $\Phi$ the meaning of an external magnetic flux). We define the ensemble averaged number of particles

$$\bar{N}(\mu) \equiv \langle N^i(\Phi, \mu) \rangle. \quad (2)$$

The flux dependence of $\bar{N}(\mu)$ is exponentially weak, hence we ignore it. We also define the mean level spacing as

$$\Delta^{-1} = \frac{\partial \bar{N}}{\partial \mu}. \quad (3)$$
We further employ the approximation
\[ \frac{\partial^k \bar{N}}{\partial \mu^k} \equiv 0 \quad \text{for} \quad k \geq 2 \] (4)
This is exact in two dimensions \( d = 2 \) and involves corrections small in \( \Delta/\mu \) in \( d \neq 2 \).

For strong CE one has
\[ N = \int d\nu^i(\epsilon, \Phi) f(\epsilon - \mu^i(\Phi)) \] (5)
where \( N \equiv \text{const.} \) and \( \mu^i(\Phi) \) is a sample and flux dependent chemical potential. Next we define the ensemble averaged chemical potential, \( \bar{\mu} \), as the solution of the following equation:
\[ N = \bar{N}(\bar{\mu}) . \] (6)

We then write the chemical potential as
\[ \mu^i(\Phi) = \bar{\mu} + \delta\mu^i(\Phi) . \] (7)

Expanding now the Fermi function in Eq. (5) and using the GCE relation, Eq. (1), one obtains
\[ N = \sum_{k=0}^{\infty} \frac{1}{k!} \left[ \frac{\partial^k}{\partial \mu^k} N(\Phi, \bar{\mu}) \right] (\delta\mu^i(\Phi))^k . \] (8)

Employing Eqs. (3), (4) and (6), we obtain the following transcendental equation for the dimensionless variable, \( X \equiv \delta\mu^i(\Phi)/\Delta \):
\[ X + \Delta^k X^k C_k = 0 , \] (9)
where
\[ C_k \equiv \frac{1}{k!} \frac{\partial^k}{\partial \mu^k} \delta N ; \quad \delta N \equiv N^i(\Phi, \bar{\mu}) - \bar{N}(\bar{\mu}) . \] (10)

We shall look for the solution of Eq. (9) in the form of the series
\[ X = \sum_{n=0}^{\infty} a_n \Delta^n . \] (11)

Substituting Eq. (10) into Eq. (9) and comparing respective orders of powers of \( \Delta \) we find
\[ a_n = \frac{(-1)^{n-1}}{n!} \left( \delta N^n \frac{\partial \delta N}{\partial \bar{\mu}} \right)^{(n-1)} , \] (12)
where \( (n - 1) \) denotes the \( (n - 1)^{st} \) derivative with respect to \( \bar{\mu} \). Finally one has a solution for \( \delta\mu^i(\Phi) \)
\[ \delta\mu^i(\Phi) \equiv \Delta \sum_{n=0}^{\infty} \frac{(-1)^{n-1}}{n!} \Delta^n \left( \delta N^n \frac{\partial \delta N}{\partial \bar{\mu}} \right)^{(n-1)} . \] (13)

This is a central result of our analysis so far, which enables us to calculate various canonical quantities. As an example we consider the situation where \( \Phi \) is an AB flux and work out the canonically averaged persistent current
\[ I_{CE}(\Phi) = \sum_{n=0}^{\infty} \frac{1}{n!} \left( \frac{\partial^n I_{GCE}}{\partial \bar{\mu}^n} \right)^n \delta \Phi^i. \] (14)

Employing a standard thermodynamic relation

\[ \frac{\partial I_{GCE}}{\partial \mu} = \frac{\partial N^i(\Phi, \bar{\mu})}{\partial \Phi}, \] (15)

and substituting Eq. (13) into Eq. (14) we finally obtain

\[ I_{CE}(\Phi) = I_{GCE}(\Phi) - \Delta \frac{\partial}{\partial \Phi} \left[ \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+2)!} \Delta^n \frac{\partial^n}{\partial \bar{\mu}^n} [\delta N^{n+2}] \right]. \] (16)

One immediately notices that all terms in this series, except the \( n = 0 \), have the form

\[ \Delta \frac{\partial}{\partial \bar{\mu}} (\ldots) \] (17)

This means that once averaged they yield a results proportional to \( \Delta/\bar{\mu} \), as the only dependence of the averaged quantities for \( \bar{\mu} \) arises from the diffusion constant \( D = \bar{\mu} \tau/m \) (we are in \( d = 2 \), so the average density of states is constant).

Equation (16) is a prototype of a relation connecting CE to a GCE average. It goes beyond the results of refs. 6-10 in that it provides a systematic way to obtain higher corrections. More generally Eq. (16) can be cast in the form

\[ \frac{\partial F}{\partial \Phi}_{CE} = \frac{\partial \Omega}{\partial \Phi}_{GCE} + \Delta \frac{\partial}{\partial \Phi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+2)!} \Delta^n \frac{\partial^n}{\partial \bar{\mu}^n} [\delta N^{n+2}] \] (18)

where \( \Phi \) now represents any static externally controlled parameter. Note that here \( \delta N \) is a grandcanonical quantity, so the canonical quantity on the l.h.s. of Eq. (18) is expressed solely by means of GCE quantities.

A simple version of Eq. (18), namely this relation where only the \( n = 0 \) term on the r.h.s. has been included, has been extensively employed [6-10] to study differences between the CE and the GCE persistent current in normal (as opposed to superconducting) rings and cylinders [15], and the anomalous paramagnetic orbital magnetism of small dots [16]. It is also interesting to consider the problem of “hybrid” ensembles, mentioned above [13,14,17].

**III. STATISTICAL ENSEMBLES: \( T > 0 \)**

So far we were interested in differences between the “canonical” and the “grandcanonical” ensembles (and hybrids thereof) due to quenched disorder statistical fluctuations. These differences are clearly manifested at \( T=0 \). The CE was represented as an ensemble of effectively grandcanonical systems, with sample specific (and flux dependent) chemical potentials. It is argued below that this is not the case at \( T > 0 \): even on the level of a specific system, and even when we consider thermodynamically averaged quantities (and not fluctuations), a canonical system cannot be replaced by an effective grandcanonical system. This will be the source to further differences between the CE and the GCE (i.e., differences beyond those discussed in Refs. 6-10,18). Here we study these difference and show that they are related to differences between statistical mechanics and thermodynamics on the mesoscopic scale.

In other words, consider an observable \( A \). Canonical and grandcanonical averages will be denoted as \( \langle A^i|\mathcal{N} \rangle \) and \( \langle A^i|\mu \rangle \) respectively. The difference between such averages can be written as
\[
\langle A^i |_N \rangle - \langle A^i |_{\mu} \rangle = \langle A^i |_{\mu(N)} \rangle - A^{(i)} |_{\mu} + \langle A^i |_N \rangle - A^{(i)} |_{\mu(N)} \rangle .
\]

(19)

The first term was the center of our discussion in Section 2. Note that if one assumes the relation
\[
\frac{\partial F^{(i)}}{\partial x} \bigg|_N = \frac{\partial \Omega^{(i)}}{\partial x} \bigg|_{\mu(N, \Phi)}
\]
(20)
(where \(\Phi\) is an externally controlled parameter) this implies that the second term on the r.h.s. of Eq. (19) vanishes. The first term on the r.h.s. exhausts, in that case, the difference between the CE and the GCE, including the temperature dependence. In general, though, as is discussed below, Eq. (20) is not satisfied exactly at \(T > 0\), implying the non-vanishing of the second term on the r.h.s. of Eq. (19). The reason is that at finite temperature the relation given in Eq. (20) above, while being exact within the framework of thermodynamics, includes correction terms when considered within the framework of statistical mechanics and applied to finite systems (see Section 3b). It follows that the fact that at finite temperatures we allow for dynamical particle fluctuations in the grandcanonical case (while no particle exchange with the reservoir is allowed under canonical constraints) affects quantities related to fluctuation terms, e.g. \(\langle \delta N^2 \rangle\). In particular this applies to the relations between GCE and CE averages, which contain fluctuation terms (cf. Eq. (18)). It is important to stress that the finite temperature difference between canonical and grandcanonical quantities, which is of a dynamical nature, exists even for sample specific quantities. This contribution is to be superimposed on top of the contribution discussed earlier, which arises due to averaging over quenched disorder.

3a Differences Between the Canonical and the Grandcanonical Ensembles: Single Particle Level Occupancy

We demonstrate the \(T > 0\) effect by studying the difference in the single particle level occupancy between canonical and grandcanonical systems. As a simple example, let us consider first a two-level system occupied by \(N = 1\) electron (in the grandcanonical case this becomes \(\bar{N} = 1\)). This is depicted in Fig. 4. Here \(\Delta\) denotes the level spacing. At \(T=0\) there is no practical difference between the canonical and the grandcanonical system. By contrast, at \(T > 0\), the probability of finding the second level occupied is given by
\[
\begin{align*}
  f_{C}(\text{level no. 2}) & = \frac{1}{e^{\beta \Delta} + 1} \quad \text{canonical} \\
  f_{GC}(\text{level no. 2}) & = \frac{1}{e^{\beta \Delta/2} + 1} \quad \text{grandcanonical}
\end{align*}
\]
(21)
(in the canonical case we use the Boltzmann factor for any given manybody state, projecting then onto the single particle state at hand; in the grandcanonical case we employ the Fermi-Dirac factor, \(f \equiv f_{GC}\). Clearly \(f_{C} \neq f_{GC}\).

We next consider a many level system. Closely related works [19] which include analytical studies of uniformly spaced spectra [20], possibly with the effect of level degeneracy [21], and a numerical study [22], have been published earlier. The Hamiltonian of the system, \(\hat{H}\), is assumed to preserve the number of particles (electrons), i.e. \([\hat{H}, \hat{N}] = 0\). The canonical partition function is given by
\[
Z_{C}^{(i)}(N) = \text{Tr}(e^{-\beta \hat{H}^{(i)}} \delta(\hat{N} - N))
\]
(22)
where the hatted quantities are operators, and the \(\text{Tr}\) is unrestricted (i.e., it includes summation over eigenstates of \(\hat{N}\) with various eigenvalues). We use the following representation of the Kroenecker delta function
\[ \delta(\hat{N} - N) = \beta \int \frac{d\mu}{2\pi i} e^{\beta \mu (\hat{N} - N)} . \] (23)

Substituting Eq. (23) into Eq. (22) we obtain

\[ Z_C(N) = \beta \int \frac{d\mu}{2\pi i} e^{-\beta \mu N} \text{Tr} e^{-\beta (\hat{H} - \mu \hat{N})}. \] (24)

Our goal now is to expand the r.h.s. of Eq. (24) around a saddle point [23-25]. To simplify the discussion we shall restrict ourselves here to systems of noninteracting fermions. We can find a diagonalizing basis in which \( \hat{H} \) can be written as

\[ \hat{H} = \sum_k \epsilon^{(i)}_k a_k^+ a_k . \] (25)

The canonical partition function is then written as

\[ Z_C^{(i)}(N) = \beta \int \frac{d\mu}{2\pi i} e^{-\beta \mu N} \prod_k (1 + e^{-\beta (\epsilon^{(i)}_k - \mu)}) \]

\[ = \int \frac{d\mu}{2\pi i} e^{N g(\mu)} , \] (26)

where

\[ g(\mu) = -\beta \mu + \frac{1}{N} \sum_k \ln (1 + e^{-\beta (\epsilon^{(i)}_k - \mu)}). \] (27)

In analogy with the grandcanonical ensemble, the single particle level occupation factor in the canonical case, \( f_C^{(i)}(\epsilon_n; N) \) is given by

\[ f_C^{(i)}(\epsilon_n; N) = \frac{1}{\beta} \frac{\partial}{\partial \epsilon^{(i)}_n} Z_C^{(i)}(N) = \frac{\int \frac{d\mu}{2\pi i} f(\epsilon^{(i)}_n - \mu) e^{N g^{(i)}(\mu)}}{\int \frac{d\mu}{2\pi i} e^{-N g^{(i)}(\mu)}}. \] (28)

At this stage we shall replace the limits of the integrals by infinite contours, \( \int \frac{d\mu}{2\pi i} \rightarrow \int_{-\infty}^{+\infty} \), and evaluate these integrals employing the stationary phase approximation. It is possible to show [27] that this procedure is sound, and that the main contribution to the integral is contained within the original interval \( \left[ \frac{-\pi}{\beta}, \frac{\pi}{\beta} \right] \) when the temperature is larger than the mean level spacing.

One may now expand the numerator and the denominator of the r.h.s. of Eq. (28) (or Eq. (24)), making use of the diagrammatic expansion outlined further below. Here we shall derive a simple approximate expression, retaining only the Gaussian term in the exponent in Eq. (28), and expanding \( f \) up to the second order \( m \mu - \mu_0^{(i)} \) (\( \mu_0^{(i)} \) is the saddle point of the expansion, see Section 3b). One then obtains (on the limit of a quasi continuous spectrum):

\[ f_C(\epsilon; N) = f(\epsilon - \mu_0^{(i)}) - \frac{\Delta}{2\beta} f''(\epsilon - \mu_0^{(i)}). \] (29)
We readily see that the canonical distribution $f_C$ is qualitatively equivalent to the grandcanonical distribution at a lower temperature. To find this effective lower temperature we write

$$f'(\mu; \beta_{GC}) = f'_C(\epsilon = \mu; N; \beta_C) = f'(\mu; \beta_C) - \frac{\Delta}{2\beta} f''(\mu; \beta_C).$$

(30)

This yields

$$\beta_{GC} \approx \beta_C \left(1 + \frac{\Delta \beta_C}{4}\right),$$

(31)

where $\beta_{GC}$ is the effective grandcanonical inverse temperature which corresponds to a canonical inverse temperature $\beta$. Based on the above discussion, the last expression is valid for $T \simeq \Delta$. It can be rewritten as

$$T_{GC} \approx \frac{T_C}{1 + \frac{\Delta}{4T_C}},$$

(32)

which in the limit of $T_C \gg \Delta$ becomes

$$T_{GC} \approx T_C - \frac{\Delta}{4}, \quad T_C \gg \Delta.$$

(33)

One may employ slightly different criteria for defining the effective temperature of the canonical distribution function (e.g., $f(\mu, \beta_{GC}) = f_C(\epsilon = \mu; N; \beta_C)$ instead of Eq. (30)). But the statement that the canonical distribution, at temperatures larger than $\Delta$, corresponds to $T_C > T_{GC}$ should remain valid. A similar shift of the effective temperature has been discussed (in the context of a uniform spectrum) in Refs. [20-22]. This also agrees qualitatively with the 2-level scenario discussed above, where the effective canonical temperature is higher by a factor of 2.

3b Differences Between the Canonical and the Grandcanonical Ensembles at $T > 0$: A General Approach

Our next step is to develop a systematic method for calculating physical observables within the canonical ensemble, accounting for finite temperature effects, in particular for the fact that at finite temperature $f_C \neq f$. We incorporate into Eq. (24) for the canonical partition function, $Z_C$, the relation

$$e^{-\beta \Omega(\mu,T,x)} = \text{Tr} e^{-\beta (\hat{H} - \mu \hat{N})},$$

(34)

writing

$$Z_C(N, T, \Phi) \approx \frac{\beta}{2\pi i} \int_{-i\infty}^{+i\infty} d\mu e^{-\beta (\Omega(\mu,T,\Phi)+\mu N)},$$

(35)

The limits of the integral have been extended to infinity, following the same arguments as in the derivation of $f_C$. We note that the expression for $Z_C$ is quite general and is valid for systems of interacting electrons as well. We shall restrict ourselves to systems of non-interacting electrons in the diffusive regime. Our goal here is to evaluate ensemble averaged thermodynamic observables within the canonical ensemble. (We stress that similar ideas may be employed for calculating other classes of observables, e.g., linear response transport coefficients).

As we have done above, we define the sample specific saddle point of the integral in Eq. (35), $\mu^{(i)}_0(T, \Phi)$ [28]
\[
\frac{\partial}{\partial \mu} \left[ \Omega^{(i)}(\mu, T, \Phi) + \mu N \right]_{\mu_0^{(i)}(T, \Phi)} = 0. \tag{36}
\]

Let us define the grandcanonical expectation value of the particle number as

\[
N^{(i)}(\mu, T, \Phi) = -\frac{\partial \Omega^{(i)}(\mu, T, \Phi)}{\partial \mu}. \tag{37}
\]

(For discussion of the relation between this identity, defined within statistical mechanics, and thermodynamic identities, we refer the reader to Section 3d). The saddle point equation then assumes the form:

\[
N^{(i)}(\mu_0^{(i)}(T, \Phi), T, \Phi) = N, \tag{38}
\]

where \( N \) is a given integer. We are supposed to solve Eq. (38) for \( \mu_0^{(i)} \), and substitute it in the expression for \( Z_C \), Eq. (35), expanding around the saddle point:

\[
\Omega^{(i)}(\mu) + \mu N = F^{(i)}(\mu_0^{(i)}) + \frac{1}{2!} \frac{\partial^2 \Omega^{(i)}}{\partial \mu^2} (\mu - \mu_0^{(i)})^2 + \cdots + \frac{1}{n!} \frac{\partial^n \Omega^{(i)}}{\partial \mu^n} (\mu - \mu_0^{(i)})^n + \cdots \tag{39}
\]

We note that \( \mu_0^{(i)} \) is real. We have used the notation \( F^{(i)}(\mu_0^{(i)}) \equiv \Omega^{(i)}(\mu_0) + \mu_0^{(i)} N \). Unfortunately the above expression, Eq. (39) is not very useful for practical purposes. Each term is to be evaluated at the chemical potential \( \mu_0^{(i)} \) which is a function of the external parameter \( \Phi \), but even more significantly, is sample specific. Evidently, it is important to perform ensemble averaging by calculating the sample specific function \( \mu_0^{(i)}(\Phi) \) for each and every member of the ensemble. Instead we replace this quantity by a (positive) constant \( \bar{\mu} \), assumed to be the result of averaging \( \mu_0^{(i)}(\Phi) \) over \( \Phi \) and over ensemble realizations, \( \bar{\mu} \equiv \langle \mu_0^{(i)}(\Phi) \rangle \). We assume that in some sense (to be discussed below) \( \bar{\mu} \) is close to \( \mu_0^{(i)}(\Phi) \). We thus distort the integration contour, \( \mathcal{C} \), of Eq. (35) which goes through the saddle point \( \mu_0^{(i)}(\Phi) \) into another contour, \( \tilde{\mathcal{C}} \), which goes through \( \bar{\mu} \). Expanding around the latter, Eq. (39) is now replaced by

\[
\Omega^{(i)}(\mu) + \mu N = F^{(i)}(\bar{\mu}) - \frac{1}{2} \frac{\partial^2 \Omega^{(i)}}{\partial \bar{\mu}^2} (\mu - \bar{\mu})^2 - \sum_{n=1}^{\infty} \left[ \frac{\partial^{n-1}}{\partial \bar{\mu}^{n-1}} \delta N^{(i)} \right] (\mu - \bar{\mu})^n. \tag{40}
\]

Here \( \delta N^{(i)} \equiv N^{(i)}(\bar{\mu}) - N \). The mean level spacing \( \Delta \) satisfies \( \Delta = \left\langle \frac{\delta N^{(i)}}{\delta \mu} \right\rangle_{\bar{\mu}}^{-1} \). In writing Eq. (40) we assumed that \( N = \frac{\bar{\mu}}{\Delta} \), such that \( \frac{\partial^n}{\partial \bar{\mu}^n} N = 0 \) for \( n \geq 2 \). Strictly speaking this is correct for a two dimensional system; for \( d \neq 2 \) we introduce errors of order \( \Delta \bar{\mu} \) or less.

Substituting the expansion, Eq. (40), into the expression for \( Z_C \), Eq. (35), we obtain

\[
Z_C^{(i)}(N, T, \Phi) = \frac{\beta}{2\pi i} e^{-\beta F^{(i)}(\bar{\mu})} \int_{\tilde{\mathcal{C}}} d\mu \frac{\delta}{\delta \bar{\mu}} (\mu - \bar{\mu})_N \exp \left\{ \beta \sum_{n=1}^{\infty} \frac{1}{n!} \frac{\partial^{n-1}}{\partial \bar{\mu}^{n-1}} \delta N^{(i)} (\mu - \bar{\mu})^n \right\}. \tag{41}
\]

We now define new variables

\[
\tau \equiv -i \sqrt{\frac{\beta}{\Delta}} (\mu - \bar{\mu}), \quad V_n^{(i)} = \frac{1}{n!} \frac{(\tau)^n}{(\beta \Delta)^{n-1} \Delta^{n-1} \frac{\partial^{n-1}}{\partial \bar{\mu}^{n-1}} \delta N^{(i)} (\bar{\mu})}, \tag{42}
\]

in terms of which we may rewrite the partition function as
\[ Z_C^{(i)}(N, T, \Phi) = \sqrt{\frac{\Delta \beta}{2\pi}} e^{-\beta F^{(i)}(\bar{\mu})} \int_{-\infty}^{\infty} \frac{d\tau}{\sqrt{2\pi}} e^{-\frac{\tau^2}{2}} \exp \left\{ \sum_{n=1}^{\infty} V_n^{(i)} \tau^n \right\}, \]  

Equation (43) is the basis of our diagrammatic expansion. We first stress that all diagrams in this expansion are to be evaluated within the grandcanonical ensemble, which is the attractive feature of our analysis. The vertex \( V_n \) should be understood in the following way: \( \delta N \) is a trace of a ring diagram with one scalar vertex (i.e. proportional to the first derivative of \( \Omega \) with respect to \( \bar{\mu} \)). Hence \( V_n \) corresponds to \( n \) scalar vertices. (One may dress such vertices by interaction lines, impurity lines, etc. as depicted in Fig. 5). We now expand the exponential in Eq. (43). We shall comment on the small parameter of the expansion below. In analogy with Wick’s theorem we are now able to define contraction with the variable \( \tau \). We shall employ the following notation: for the second order term in \( \tau \) we write

\[ \langle \tau \tau \rangle \equiv \int \frac{d\tau}{\sqrt{2\pi}} e^{-\frac{\tau^2}{2}} \cdot \tau^2 = 1. \]  

This defines the combinational factor that comes with this term (=1), corresponding to the fact that there is only one way of contraction. For the fourth order term in \( \tau \) we write

\[ \langle \tau\tau\tau\tau \rangle \equiv \int \frac{d\tau}{\sqrt{2\pi}} e^{-\frac{\tau^2}{2}} \tau^4 = 3. \]  

The combinational factor associated with this term is 3, corresponding to 3 possibilities of contraction. In these “contractions” the role of the zeroth order propagation is played by \( e^{-\frac{\tau^2}{2}} \). In our diagrammatic representation we shall use a zig-zag line for this propagator. We stress that the only role of this statistical \( \tau \)-propator is to account for combinatorial factors. It does not carry any momentum or energy. We also note that odd powers of \( \tau \) vanish.

To evaluate thermodynamic derivatives we need to calculate \( \log Z_C \). To this end we may employ the linked cluster expression (including statistical lines!) whereby only linked diagrams are to be accounted for (cf. e.g. Ref. 29). We thus may write

\[ F^{(i)}(N, T, \Phi) = F^{(i)}_{TD}(\bar{\mu}, T, \Phi) - \frac{1}{\beta} \log \sqrt{\frac{\Delta \beta}{2\pi}} - \{ \text{all connected diagrams} \}^{(i)}. \]  

Anticipating the discussion of the next section, pertaining to differences between statistical mechanical and thermodynamic quantities, we use the notation

\[ F^{(i)}_{TD}(\bar{\mu}, T, \Phi) \equiv \Omega^{(i)}(\bar{\mu}, T, \Phi) + \bar{\mu}N. \]  

The first term on the r.h.s. of Eq. (46) yields the sample specific grandcanonical contribution. The second term, due to Gaussian fluctuations around the expansion point (not the saddle point!) \( \bar{\mu} \), is a temperature-dependent sample-independent contribution. All the other terms are, in principle, sample specific. The quantity \( \Omega^{(i)}(\bar{\mu}, T, \Phi) \) may be evaluated employing the standard linked cluster expansion [30], which does not include statistical lines. The r.h.s. of Eq. (46) yields terms which are particular to the canonical ensemble.

At this point we can formulate the rules for constructing canonical diagrams. We consider a linked diagram consisting of \( p \) electronic loops (with \( n_1, n_2, \ldots n_p \) scalar vertices respectively). The total number of vertices must be even \( n_1 + n_2 + \ldots + n_p = 2K \). As all these vertices are connected by statistical lines, it follows that \( K \) is the number of such lines, \( K \geq p - 1 \).
1. With each statistical line associate a factor \((-\Delta)\).
2. With each electronic loop which contains \(n_i\) vertices associate a factor 
\[\frac{1}{n_i!} \frac{\partial^{n_i-1}}{\partial \bar{\mu}^{n_i-1}} \delta N(\bar{\mu}).\]
3. Any subset of \(m\) loops which consist of the same number of vertices carries a factor \(\frac{1}{m!}\).
4. Each diagram carries a factor \(T^w, w = K - p + 1\).
5. With each diagram associate a combinatorial factor, representing the number of different ways of constructing it. \((48)\)

We stress that the numerical factors obtained through the contractions discussed above correspond, in the present language, to the number of different ways of connecting scalar vertices by statistical lines. Hence, the only role of the statistical lines is to provide the right counting of diagrams. We also stress that the temperature factor \(T^w\) associated with each diagram (see rule no. 4 above) does not exhaust the temperature dependence of that particular diagram. The latter usually contains further important temperature dependence.

We shall nevertheless use this power of \(T\) to classify the diagrams into different families, characterized by the index \(w\). Examples are depicted in Figs. 6 and 7. It is understood that disorder averaging has to be carried out subsequently. At zero temperature only the \(w = 0\) family survives. It is easy to see that these diagrams originate from the linear term in Eq. (40). An expansion about the true saddle point, \(\mu_0^{(i)}(T, \Phi)\) would not reproduce these diagrams. It turns out that these are the contributions which describe differences between the CE and the GCE at \(T = 0\), cf. Section 2. They are obtained when Eq. (20) is assumed to hold, and each member of the canonical ensemble is assigned an effective, sample specific chemical potential. The \(w = 0\) family represents contributions due to quenched disorder (as in Refs. [6-10,14]) but not due to differences between statistical mechanics and thermodynamics (see Section 3d). After some algebra one obtains (hereafter we suppress the index \((i)\) and consider only ensemble averaged quantities)

\[\langle \delta F_{w=0} \rangle = -\sum_{n=1}^{\infty} \frac{\delta^n}{(n+1)!} \frac{\partial^{n-1}}{\partial \bar{\mu}^{n-1}} \langle \delta N^{n+1} \rangle.\] \((49)\)

Derivation of Eq. (59) with respect to an external parameter, \(\Phi\), yields Eq. (18) \([14]\). The first \((n = 1)\) term in the sum corresponds to the two loop diagram in Fig. 6. Upon averaging over (diffusive) disorder, it yields the Altshuler-Shklovskii term \([4]\), which was employed in Ref. [6-10]. The \(n \geq 2\) terms include complete derivatives with respect to \(\bar{\mu}\), and are negligible upon averaging (being small in the parameter \(\Delta/\bar{\mu}\)). This provides us with a posteriori justification of the diagrammatic expansion: sample specific terms in this expansion are not necessarily small, but the ensemble average is well-behaved.

We next include the \(w \geq 1\) families too. It can be shown that for the regime where we employ our expansion, \(T > \Delta\), the leading term (in \(\Delta/T\)) of each family is represented by a two-loop diagram (cf. Figs. 6,7). Evaluation of these diagrams (neglecting full derivatives with respect to \(\bar{\mu}\)) results in

\[\langle \delta F_{two-loop} \rangle = \frac{\Delta}{2} \sum_{w=0}^{\infty} \frac{(\Delta T)^w}{(w+1)!} \left\langle \left( \frac{\partial^w \delta N}{\partial \bar{\mu}^w} \right)^2 \right\rangle.\] \((50)\)
The $w = 0$ term is the Altshuler-Shklovskii quenched disorder contribution [4].

3c Relation to Spectral Correlations: Persistent Current and Heat Capacity

The summation in Eq. (50) is clearly related to correlations in the spectra of finite size disordered systems. We define the correlator $K$ and its Fourier transform $\tilde{K}$:

$$K(\epsilon - \epsilon') \equiv \Delta^2 \langle (\nu(\epsilon)\nu(\epsilon')) \rangle - \langle \nu(\epsilon) \rangle \langle \nu(\epsilon') \rangle \equiv \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \tilde{K}(t) e^{it(\epsilon - \epsilon')/\Delta},$$

(51)

where $\nu(\epsilon)$ is the sample specific density of states and $t$ is the dimensionless time (in units of $\hbar/\Delta$). We can write

$$\left\langle \left( \frac{\partial w}{\partial \mu} \delta N \right)^2 \right\rangle = \frac{\partial w}{\partial \mu} \frac{\partial w}{\partial \mu'} \int_{-\infty}^{+\infty} \frac{d\epsilon' d\epsilon}{\Delta^2} f(\epsilon - \mu) f(\epsilon' - \mu') K(\epsilon - \epsilon') \bigg|_{\mu' = \mu},$$

(52)

where $f$ is the Fermi-Dirac function. Changing variables to $\xi \equiv \epsilon - \epsilon'$, $\eta \equiv (\epsilon + \epsilon')/2$, performing the integral over $\eta$, and Fourier transforming with respect to $\xi$, we obtain

$$\langle \delta F_{\text{two-loop}} \rangle = \frac{\pi T}{2} \sum_{w=0}^{\infty} \frac{1}{(w + 1)!} \left( \frac{\Delta}{T} \right)^w \int_0^\infty dt \frac{t^{2w}}{\sinh^2 \pi t} \tilde{K} \left( \frac{\Delta}{T} \right).$$

(53)

Equations (46) and (53) form the basis for the analysis of the various corrections to the GCE averages, and depict the dependence of these corrections on spectral correlations. We study two examples comparing the $w = 0$ (quenched disorder contribution) and $w = 1$. We consider the case of diffusive disorder.

The average persistent current in the canonical ensemble, $\langle I \rangle_{\text{CE}}$, is obtained by deriving $\langle F \rangle$ with respect to the Aharonov-Bohm flux, $\Phi$. The flux dependent part of the time correlator for quasi-one-dimensional rings is given by

$$\tilde{K}(t) = \frac{|t|}{\pi} \sqrt{\frac{1}{4\pi g|t|}} \sum_{p=1}^{\infty} e^{-\frac{\pi^2}{4p^2}} \cos \frac{4\pi p\Phi\Phi_0}{\Phi_0},$$

(54)

where $g = E_c/\Delta \gg 1$ is the dimensionless conductance ($E_c$ is the Thouless correlation energy) and $\Phi_0 = \hbar c/e$. Only even harmonics appear in Eq. (54). Expanding $\langle I \rangle_{\text{CE}} = \Sigma_{p=1}^{\infty} 4\pi p \sin 4\pi p\Phi/\Phi_0$, we find that the quenched disorder contribution ($w = 0$) is [6-10]

$$I_p^{\text{dis}} = \frac{\Delta}{\Phi_0} \left\{ \begin{array}{ll}
\frac{2}{p^2} T_{E_c} e^{-\sqrt{\frac{\pi^2}{4p^2}}} & \Delta < T < E_c/p^2, \\
0 & T > E_c/p^2.
\end{array} \right.$$

(55)

We shall denote the leading $w = 1$ contribution with a superscript $SM - TD$. The rationale behind that will become evident in the next section. We obtain

$$I_p^{\text{SM-TD}} = \frac{\Delta}{\Phi_0} \left\{ \begin{array}{ll}
\frac{1}{g} \frac{15\sqrt{2\pi} e^{(5/2)\sqrt{E_c}/p}}{24}\pi T_{E_c} & \Delta < T < E_c/p^2, \\
\frac{1}{16\pi^4 p^4 T_{E_c}} e^{-\sqrt{\frac{\pi^2}{4p^2}}} & T > E_c/p^2.
\end{array} \right.$$  

(56)

The average canonical heat capacity $\langle \langle C \rangle_{\text{CE}} \rangle$. It is given by $\langle C \rangle_{\text{CE}} = -\beta^2 \partial^2 (\beta\langle F \rangle) / \partial \beta^2$ and is written as a sum of contributions (cf. Eq. (46)):

$$\langle C \rangle_{\text{CE}} = \langle C \rangle_{\text{GCE}} + \langle \delta C^{\text{Gauss}} \rangle + \langle \delta C^{\text{dis}} \rangle + \langle \delta C^{\text{SM-TD}} \rangle.$$  

(57)
The first term is the grandcanonical contribution, which for a degenerate gas of non-interacting electrons is $\frac{\pi^2}{3} T D$. The term due to Gaussian fluctuations yields $-\frac{1}{2}$. This contribution can be reinterpreted when $T > \Delta$ as a shift of the grandcanonical temperature ($T > \Delta$) towards a lower temperature $T \to T - \frac{3}{2\pi^2} \Delta$ forced by the canonical constraints. This is qualitatively similar to the shift found in Section 3a, in the context of the single level occupation function. A similar shift in the heat capacity was found in Ref. [20] (see also Refs. [21,22]). The next terms in Eq. (57) are evaluated employing Eq. (53). We are interested in energies larger than $\Delta$, hence $t < 1$. The time correlator has two interesting regimes (random matrix theory and Altshuler-Shklovskii [4] respectively):

$$\tilde{K}(t) = \frac{\langle t \rangle}{b\pi} \left\{ \begin{array}{ll} \frac{1}{4\pi g(|t|)}^{-d/2} & g^{-1} < t < 1 \\ \Delta_{\tau_e} < t < g^{-1} \end{array} \right.,$$

where $b = 1, 2, 4$ for the orthogonal, unitary and symplectic ensembles respectively. Here $\tau_e$ is the elastic mean free time. Eq. (58) does not account for the crossover regimes. It leads to

$$\langle \delta C^{\text{dis}} \rangle = \frac{1}{b\pi} \frac{\Delta}{T} \left\{ \begin{array}{ll} \frac{1}{\pi} \left( \frac{T}{E_c} \right)^{d/2} & \Delta < T < E_c \\ \eta_d \left( \frac{T}{E_c} \right)^{d/2} & T > E_c \end{array} \right.,$$

and in the leading order in $\Delta/T$ [31]

$$\langle \delta C^{\text{SM-TD}} \rangle = \frac{1}{b\pi} \left( \frac{\Delta}{T} \right)^{d/2} \left\{ \begin{array}{ll} \frac{3\zeta(3)}{4\pi} \eta_d \left( \frac{T}{E_c} \right)^{d/2} & \Delta < T < E_c \\ & T > E_c. \end{array} \right.$$

In this example the $SM - TD$ contribution is parametrically smaller than the contribution due to quenched disorder.

### 3d Differences Between Statistical Mechanics and Thermodynamics

Previous studies of differences between the GCE and the CE used the thermodynamic identity, Eq. (20) as a starting point. This implies that for any specific realization, a canonical system can be replaced by an equivalent grandcanonical system with an effective chemical potential which depends on disorder and on the value of the relevant external parameters ($\Phi$). Physical observables, though, should be evaluated within the framework of statistical mechanics. While Eq. (20), considered as a thermodynamic relation, is exact – by construction, a statistical mechanics relation between $F$ and $\Omega$ contains important corrections, cf. Eq. (46). These corrections are expected to be suppressed in the “thermodynamic limit” – at high enough temperatures and/or large enough system’s size.

These types of corrections (deviations from the thermodynamic relation, Eq. (20)) may be quite important on the mesoscopic scale. Thus, the expansion outlined above includes two qualitatively different classes of contributions: (a) the $w = 0$ family, which assumes the validity of Eq. (20), and accounts for differences between the CE and the GCE due to quenched disorder; (b) the $w \geq 1$ families, which account for deviations (within statistical mechanics) from the thermodynamic identities. (This is the rationale behind the notation used in Eqs. (56), (57) and (60)). The two-loop term of the $w = 1$ family is the leading contribution (in $\Delta/T$) of this class.

Coming now to the examples discussed in the previous section, we note that the “$SM - TD$” contributions are smaller than those due to quenched disorder. It is interesting to note, though, that the former is quite robust as function temperature: contrary to what might be a naive expectation, contributions due to differences between statistical mechanics are not suppressed on the scale $T \sim \Delta$. In the case of the persistent current the “$SM - TD$” contribution
(Eq. (56)) decreases algebraically with temperature up to $T \sim E_c \gg \Delta$, and is then suppressed exponentially. In the case of the heat capacity it is also suppressed algebraically (up to $T \sim \hbar/\tau_{ef}$). Our analysis underlines the relation between the “$SM - TD$” contributions and spectral correlations.

Acknowledgements

We have benefited from discussion with J. Hajdu, Y. Imry, A. Schmid and A.D. Stone. This research was supported by the German-Israel Foundation (GIF), the U.S.-Israel Binational Science Foundation (BSF) and the Israel Academy of Sciences.
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**Figure Captions**

**Fig. 1:** Four different thought experiments leading to different definitions of $\delta N$ (see text).

**Fig. 2:** Fluctuations in the number of electrons done to quenched disorder. (a) $\delta N^{(3)}$: At zero temperature members (1), (2) and (3) of the ensemble (differing in their respective shapes, impurity configurations, etc.) will have 3, 4 and 2 electrons, respectively. (b) $\delta N^{(4)}$: Fluctuations in $N$ due to variations of an external parameter, $\Phi$. The equilibrium values of $N$ at $\Phi_1$, $\Phi_2$ are 3, 2, respectively.

**Fig. 3:** Empty-occupied levels near the Fermi energy, (a) GCE; (b) CE. Enhanced probability for chemical potential to fall in a narrow gap.

**Fig. 4:** A two-level system under (a) canonical, (b) grandcanonical constraints. There are no observable differences at $T = 0$.

**Fig. 5:** A contribution to $V_5$. Solid lines denote electron propagators; wiggly lines – electron-electron interactions; dashed lines – impurity scattering.

**Fig. 6:** The $w = 0$ family of skeleton canonical diagrams with $K = 1, 2, 3$. Zigzag lines are “statistical lines”; full lines – electron propagators; black dots – scalar vertices. The first diagram yields the Altshuler-Shklovskii result upon averaging over disorder.

**Fig. 7:** Skeleton diagrams of the $w = 1$ family (up to $K = 3$).