Effects of Sample Specific Variations and Fluctuations of Thermal Occupancy on Fluctuations of Thermodynamic Quantities

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Abstract

Standard results for the fluctuations of thermodynamic quantities are derived under the assumption of sampling identical systems that are in different, not fully equilibrated states. These results apply to fluctuations with time in a particular macroscopic body and can be traced to the fluctuations of thermal occupancy. When many identically prepared - but not identical - systems are studied, mesoscopic fluctuations due to variations from sample to sample contribute to the fluctuations of thermodynamic quantities. We study the combined effect of mesoscopic fluctuations and fluctuations of thermal occupancy. In particular, we evaluate the total particle number and specific heat fluctuations in a two-dimensional, non-interacting electron gas in classically integrable and chaotic circumstances.
I. INTRODUCTION

The state of thermal equilibrium of a closed system is achieved when its entropy is at maximum. In this state, the thermodynamic quantities characterizing macroscopic bodies that comprise it are at their mean values (thermodynamic averages). Thermodynamic fluctuations are the deviations of these quantities from their mean values and are described by the Einstein formula for the probability density:

$$w(x) = const \exp [S(x)]$$

where $S(x)$ is the entropy and $x = \{x_1, x_2, \ldots, x_n\}$ are the thermodynamic quantities. Ultimately, these fluctuations can be related to the fluctuations of thermal occupancy. For instance, thermal occupancy of quantum gases can be derived starting with a generally non-equilibrium state, followed by maximization of entropy subject to constraints (conserved quantities).

This approach to fluctuations, however, neglects sample-specific variations: it assumes that sampling occurs in the ensemble of identical systems that are in different states, slightly away from the equilibrium. On the other hand, it has become abundantly clear over the last half-century that sample-specific variations are an important source of fluctuations, as witnessed by developments in mesoscopic physics. These must be included when thermodynamic properties of many identically prepared, yet not identical, systems are studied. In this work we investigate the combined contribution of mesoscopic fluctuations and fluctuations of thermal occupancy to fluctuations of thermodynamic quantities.

We use a simple formalism that gives fluctuations of thermodynamic quantities as a sum of two terms: the first due to thermal occupancy fluctuations and the second due to sample-specific fluctuations. The latter is expressed in terms of the correlation function of the density of energy levels. The results are illustrated for the fluctuations of the number of particles and of the specific heat in systems with the fixed chemical potential and volume. As a model system, we use the degenerate, two-dimensional, non-interacting electron gas with level statics corresponding to classically chaotic and integrable motions respectively.
II. FORMALISM

In the most general form, the value of a thermodynamic quantity, whose density is expressed as a function of energy, can be computed as the integral over the spectrum

\[ G = \int d\varepsilon \rho(\varepsilon) f(\varepsilon) g(\varepsilon) \]  

(1)

where \( \rho(\varepsilon) \) level density and \( f(\varepsilon) \) is the thermal occupancy. Under an obvious assumption that \( \rho \) and \( f \) are uncorrelated variables, we find the following expressions for the mean and the variance

\[ \overline{G} = \int d\varepsilon \rho(\varepsilon) \overline{f}(\varepsilon) g(\varepsilon) \]  

(2)

\[ \delta G^2 = \delta G^2_\rho + \delta G^2_f \]  

(3)

\[ \delta G^2_\rho = \int \int d\varepsilon_1 d\varepsilon_2 \delta \rho(\varepsilon_1) \rho(\varepsilon_2) \overline{f}(\varepsilon_1) \overline{f}(\varepsilon_2) g(\varepsilon_1) g(\varepsilon_2) \]  

(4)

\[ \delta G^2_f = \int \int d\varepsilon_1 d\varepsilon_2 \overline{\rho}(\varepsilon_1) \overline{f}(\varepsilon_1) \delta f(\varepsilon_2) g(\varepsilon_1) g(\varepsilon_2) \]  

(5)

where the over-bar stands for a mean value. Using

\[ \delta f(\varepsilon) = \frac{\partial \overline{f}(\varepsilon)}{\partial \mu} \left( \frac{\partial \overline{N}}{\partial \mu} \right)^{-1} \delta N + \frac{\partial \overline{f}(\varepsilon)}{\partial T} \delta T \]  

(6)

where \( \mu \) is the chemical potential and \( T \) is temperature, we find

\[ \delta f(\varepsilon_1) \delta f(\varepsilon_2) = \frac{\partial \overline{f}(\varepsilon_1)}{\partial \mu} \frac{\partial \overline{f}(\varepsilon_2)}{\partial \mu} \left( \frac{\partial \overline{N}}{\partial \mu} \right)^{-2} \delta N^2_f + \frac{\partial \overline{f}(\varepsilon_1)}{\partial T} \frac{\partial \overline{f}(\varepsilon_2)}{\partial T} \delta T^2 \]  

(7)

Combining eqs. (2), (5) and (7), we find, as expected from \( \delta G_f = (\partial \overline{G}/\partial N) \delta N + (\partial \overline{G}/\partial T) \delta T \),

\[ \overline{\delta G^2_f} = \left( \frac{\partial \overline{G}}{\partial \mu} \right)^2 \left( \frac{\partial \overline{N}}{\partial \mu} \right)^{-2} \delta N^2_f + \left( \frac{\partial \overline{G}}{\partial T} \right)^2 T^2 \]  

(8)

\[ = T \left( \frac{\partial \overline{C}}{\partial \mu} \right)^2 \left( \frac{\partial \overline{N}}{\partial \mu} \right)^{-1} + \left( \frac{\partial \overline{C}}{\partial T} \right)^2 T^2 \overline{C} \]  

(9)

where \( \overline{C} \) is the mean specific heat and we used the well-known results from the theory of thermodynamic fluctuations\[2]\n
\[ \overline{\delta N_f} = T \frac{\partial \overline{N}}{\partial \mu}, \quad \overline{\delta T^2} = \frac{T^2}{\overline{C}} \]  

(10)

to obtain the second equality. Applying this result to the fluctuations of the specific heat, for instance, we find

\[ \overline{\delta C_f^2} = T \left( \frac{\partial \overline{C}}{\partial \mu} \right)^2 \left( \frac{\partial \overline{N}}{\partial \mu} \right)^{-1} + \left( \frac{\partial \overline{C}}{\partial T} \right)^2 T^2 \overline{C} \]  

(11)
III. FLUCTUATIONS IN A 2D ELECTRON GAS

We apply the above results to a non-interacting, degenerate, two-dimensional electron gas occupying area $A$. In this case

$$\tau(\varepsilon) = \frac{\partial N}{\partial \mu} = \frac{mA}{2\pi\hbar^2} = \Delta^{-1}$$

is a constant inverse average level spacing and $m$ is the electron mass. Using standard low-temperature (Sommerfeld) expansion, we find $\mu - \varepsilon_F \approx -T \exp(-\varepsilon_F/T)$, where $\varepsilon_F$ is the Fermi energy, and

$$\bar{\delta N}_f^2 = \frac{T}{\Delta}, \quad \bar{\delta C}_f^2 = \bar{C} \approx \frac{\pi^2}{3} \frac{T}{\Delta}$$

Next, we proceed to evaluate $\bar{\delta N}_p^2$ and $\bar{\delta C}_p^2$ for the classically chaotic and integrable circumstances respectively and compare those to $\bar{\delta N}_f^2$ and $\bar{\delta C}_f^2$.

To simplify calculation, we assume a unitary ensemble (broken time reversal symmetry) in the classically chaotic case

$$\delta \rho(\varepsilon) \delta \rho(\varepsilon + \omega) = \delta (\omega) \frac{\sin^2(\pi \omega/\Delta)}{\pi \omega^2}$$

We also use a simplified ansatz in the classically integrable case

$$\delta \rho(\varepsilon) \delta \rho(\varepsilon + \omega) = \delta (\omega) \frac{\sin \left(2\pi \omega/E_m\right)}{\pi \omega \Delta}$$

Here $E_m$ is the the energy scale corresponding to the shortest classical periodic orbit. In a square well, for instance, $E_m = \sqrt{\pi \varepsilon \Delta}$. The simplified ansatz neglects large oscillations of the density correlation function for $\varepsilon >> E_m$. These should be of little consequence at finite temperatures since harmonics with incommensurate frequencies will be mixed it to wash out the effect of such oscillations. Still, unlike in the chaotic case, the correlation function depends on $\varepsilon$ via $E_m$. However, due to relevant $\varepsilon$’s being restricted to the interval of order $T$ around $\varepsilon_F$, we can replace $\varepsilon \to \varepsilon_F$

$$E_m \approx \sqrt{\pi \varepsilon \varepsilon_F \Delta}$$

With this substitution, it will be shown below that for $T \ll E_m$ the result for integrable systems is due to the delta function term in (15). Conversely, for $T \gg E_m$, the full oscillatory behavior of the level correlation function discussed in Ref. should be of little consequence since their scale is defined by $E_m$. This reasoning is ultimately confirmed by numerical
evaluation using the full form of the correlation function \([5]\) (with substitution \(\varepsilon \rightarrow \varepsilon_F\)), which yields results that are extremely close to the analytical results for \(\delta N_p^2\) obtained below using \((15)\).

To eliminate temperature-independent divergencies, we evaluate

\[
\frac{\partial \delta N_p^2}{\partial T} = \int \int d\varepsilon_1 d\varepsilon_2 \frac{\partial \rho(\varepsilon_1) \partial \rho(\varepsilon_2)}{\partial T} \left[ f(\varepsilon_1) (f(\varepsilon_2) - 1) \right]
\]

(17)

where we used that \(\int d\varepsilon_2 \partial \rho(\varepsilon_1) \partial \rho(\varepsilon_2) = 0\). Changing variables to \(\varepsilon = (\varepsilon_1 + \varepsilon_2)/2\), \(\omega = \varepsilon_2 - \varepsilon_1\) and integrating on \(\varepsilon\), we find

\[
\frac{\partial \delta N_p^2}{\partial T} = -\int_{-\infty}^{\infty} d\omega \partial \rho(\varepsilon) \partial \rho(\varepsilon + \omega) H\left(\frac{\omega}{T}\right)
\]

(18)

where

\[
H(x) \equiv \left[\frac{x}{2} \operatorname{csch}\left(\frac{x}{2}\right)\right]^2
\]

(19)

We first substitute \((14)\), \((15)\) and \((19)\) into \((17)\) and evaluate the integrals analytically. Further integration on \(T\) gives

\[
\left(\frac{\delta N_p^2}{\Delta}\right)_{\text{ch}} = \left(\frac{\delta N_p^2}{\Delta}\right)_{\text{ch}, T=0} - \frac{T}{\Delta} + \frac{1}{2\pi^2} \log\left(\frac{\sinh(2\pi^2 T/\Delta)}{2\pi^2 T/\Delta}\right)
\]

(20)

and

\[
\left(\frac{\delta N_p^2}{\Delta}\right)_{\text{in}} = \left(\frac{\delta N_p^2}{\Delta}\right)_{\text{in}, T=0} - \frac{T}{\Delta} + \frac{T}{\Delta} \coth\left(\frac{2\pi^2 T}{E_m}\right) - \frac{E_m}{2\pi^2 \Delta}
\]

(21)

for classically chaotic and integrable systems respectively, with \(E_m\) given by \((16)\) and zero-temperature fluctuations given by

\[
\left(\frac{\delta N_p^2}{\Delta}\right)_{T=0} = \int_0^{\varepsilon_F} \int_0^{\varepsilon_F} d\varepsilon_1 d\varepsilon_2 \partial \rho(\varepsilon_1) \partial \rho(\varepsilon_2)
\]

(22)

The latter is simply the variance of the number of levels over the Fermi sea and we use the results for the level number fluctuations from Ref.\([5]\) to find

\[
\left(\frac{\delta N_p^2}{\Delta}\right)_{\text{ch}, T=0} \sim \log\left(\frac{\varepsilon_F}{\Delta}\right)
\]

(23)

and

\[
\left(\frac{\delta N_p^2}{\Delta}\right)_{\text{in}, T=0} \sim \frac{E_m}{\Delta} \sim \sqrt{\frac{\varepsilon_F}{\Delta}}
\]

(24)

for classically chaotic and integrable systems respectively.
Combining now with (13), we find for the total particle number fluctuation $\delta N^2 = \delta N^2_{\rho} + \delta N^2_f$

\[
\left( \delta N^2 \right)_{ch} - \left( \delta N^2_{\rho} \right)_{ch,T=0} = \frac{1}{2\pi^2} \log \left( \frac{\sinh \left( 2\pi^2 T / \Delta \right)}{2\pi^2 T / \Delta} \right)\]

\[
\approx \frac{\pi^2 T^2 / 3 \Delta^2}{T / \Delta} - \log \left( 4\pi^2 T / \Delta \right) / 2\pi^2, \quad T \ll \Delta / 2\pi^2
\]

(25)

and

\[
\left( \delta N^2 \right)_{in} - \left( \delta N^2_{\rho} \right)_{in,T=0} = \frac{T}{\Delta} \coth \left( \frac{2\pi^2 T}{E_m} \right) - \frac{E_m}{2\pi^2 \Delta}
\]

\[
\approx \frac{2\pi^2 T^2 / 3 E_m \Delta}{T / \Delta - E_m / 2\pi^2 \Delta}, \quad T \ll E_m / 2\pi^2
\]

(27)

(28)

for classically chaotic and integrable systems respectively. Notice, that for temperatures below the energy scale where level rigidity sets in [4,5] - $\Delta$ for classically chaotic and $E_m$ for classically integrable systems - the main effect of temperature is to reduce sample specific fluctuations of the number of particles relative to the zero-temperature limit. Furthermore,
the temperature-dependent part of such fluctuations largely cancels the fluctuations (13) due to thermal occupancy. Incidentally, since in this limit the temperature-dependent sample-specific fluctuations are dominated by the \( \delta \)-function term in (14) and (15), the temperature-dependent particle number fluctuation can be found directly from

\[
\frac{\partial \delta N_p^2}{\partial T} = \frac{\partial}{\partial T} \int_0^\infty \int_0^\infty d\varepsilon_1 d\varepsilon_2 \delta \rho(\varepsilon_1) \delta \rho(\varepsilon_2) f(\varepsilon_1) f(\varepsilon_2) = \frac{1}{\Delta} \frac{\partial}{\partial T} \int_0^\infty d\varepsilon \varepsilon^2(\varepsilon) \simeq -\frac{1}{\Delta} \tag{29}
\]

confirming the results in (20) and (21). Conversely, for temperatures above the level rigidity scale, fluctuations due to thermal occupancy dominate.

Fluctuations of the specific heat (heat capacity) can be found from

\[
\delta C_p^2 = \int \int d\varepsilon_1 d\varepsilon_2 \delta \rho(\varepsilon_1) \delta \rho(\varepsilon_2) \frac{\partial f(\varepsilon_1)}{\partial T} \frac{\partial f(\varepsilon_2)}{\partial T} = T \int \int d\omega \delta \rho(\varepsilon) \delta \rho(\varepsilon + \omega) F\left(\frac{\omega}{T}\right) \tag{30}
\]

where

\[
F(x) \equiv \frac{1}{120} \left[ x \left(14\pi^4 + x^4\right) \coth\left(\frac{x}{2}\right) - 4 \left(7\pi^4 + 5\pi^2 x^2\right)\right] \text{csch}^2\left(\frac{x}{2}\right) \tag{31}
\]

and is plotted in Fig. (11). As a result we find the limiting behavior of the fluctuations

\[
(\delta C_p^2)_{ch} \approx a T/\Delta, \quad T \ll \Delta
\]

\[
\quad b (2\pi^2)^{-1}, \quad T \gtrsim \Delta \tag{32}
\]
FIG. 3: $(\delta C_p^2)_{in}$ vs. $T/E_m$, with limiting behavior (34) shown as thin straight line.

where the constants $a$ and $b$ are given by

$$a = F(0) \approx 0.997, \quad b = \int_{-\infty}^{\infty} dx \frac{[F(0) - F(x)]}{x^2} \approx 1.067$$  \hspace{1cm} (33a)

and

$$(\delta C_p^2)_{in} \approx aT/\Delta, \quad T \ll E_m$$  \hspace{1cm} (34)

for classically chaotic and integrable systems respectively. Clearly, the specific heat due to sample-to-sample variations in integrable systems has, over the large range of temperatures, the same functional dependence as that due to the fluctuations of thermal occupancy.

We show the plots of $(\delta C_p^2)_{ch}$ and $(\delta C_p^2)_{in}$ vs. $T$ in Figs. 2 and 3 respectively. Some of the curvature in these plots can be traced to that in Fig. 1. Small bumps and dips on the line in Fig. 3 is due to poor numerical convergence of rapidly oscillating integrals. For $T \gtrsim E_m$, $(\delta C_p^2)_{in}$ shows faster than exponential decay, as expected from integration of an exponentially decaying function (31) with a function rapidly oscillating around zero. In contrast with chaotic systems, in integrable systems the decay of fluctuations of the specific heat at high temperature is consistent with the greater level rigidity at larger energy scales,
as discussed in Ref. [5].

IV. CONCLUSIONS

We showed that the fluctuations of thermodynamic quantities can be separated into those that are due to sample-to-sample (mesoscopic) fluctuations and those due to thermal occupancy fluctuations. For a 2D non-interacting degenerate electron gas, both effects were included in evaluation of the particle number and specific heat fluctuations for classically chaotic and integrable cases. In the integrable case, the specific heat fluctuations due to either effect are comparable over a wide range of temperatures. For the particle number fluctuation, the temperature-dependent part of mesoscopic fluctuations is negative and, for temperatures below the energy rigidity scale, largely cancels the fluctuation due to thermal occupancy fluctuations. For higher temperatures, the latter dominates the temperature-dependent part of the fluctuation.

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