Finite size effects in canonical Fermi systems

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Abstract
I investigate the thermodynamic equivalence between finite systems of constant density of states below the Bose–Einstein condensation temperature. I show that in order to preserve the equivalence, a phenomenon called Fermi condensation has to be taken into account. This phenomenon leads to a correction of the intensive parameters of the Fermi gas and of the Fermi distribution in canonical Fermi systems at low temperatures.

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1. Introduction

Two systems under canonical conditions and with the same number of particles are called *thermodynamically equivalent* if their heat capacities are the same at any temperature and any particle number [1, 2]. If we take as a variable in the entropy function the temperature instead of the total energy, then the equality of the heat capacities implies the equality of the entropies of the two systems. The thermodynamic equivalence splits the set of all physical systems into equivalence classes. Notorious among these classes are the ones formed by ideal Bose and Fermi gases of equal and constant density of single-particle states (DOS) [3–5]. To make this more precise, a Bose and a Fermi gas of the same constant DOS have the same heat capacity at constant volume and the same entropy as a function of temperature. Although it was first proved a long time ago [3], this peculiar property of gases in two dimensions (2D) has received the deserved attention only relatively recently [1, 2, 8, 9, 14, 17, 19–21]. The thermodynamic equivalence appears now less peculiar, after Lee introduced a unified description of Bose and Fermi gases in terms of polylogarithmic functions [1] and one-to-one mappings between microscopic configurations of bosons to microscopic configurations of fermions with the same excitation energies were found [2, 9].

Moreover, it was shown that also systems of particles which obey a generalization of the Pauli exclusion principle [10] (so-called *fractional exclusion statistics*–FES) have a heat capacity that does not depend on the exclusion statistics [15]. In this way, the equivalence classes of bosons and fermions with the same constant DOS are extended and

their thermodynamical descriptions in terms of polylogarithmic functions, as given by Lee [1], are bridged together by the general description of the continuous set of FES systems [2].

Based on the mapping between microscopic configurations of bosons and fermions the notion of *Fermi condensate* was introduced [11] and a new kind of ensemble equivalence—based on the population of the Fermi condensate and its fluctuation—was proposed [12]. In [22], it was shown that canonical and grand-canonical fluctuation of the Fermi condensate in a constant DOS system are the same in the thermodynamic limit.

In [20], Pathria examined critically the thermodynamic equivalence between Bose and Fermi gases and concluded that it should not hold below the 2D Bose–Einstein condensation temperature (which is different from zero for finite systems).

In this paper, after presenting briefly the Fermi condensation and both, macroscopic and microscopic equivalence between ideal Bose and Fermi gases with constant DOS, I will show that the Fermi condensate produces a small shift of the chemical potential in the canonical Fermi system. This shift re-establishes the thermodynamic equivalence of the two gases at low temperatures.

2. Fermi condensation

Let a system $\mathcal{S}$ be in contact with a heat and particle reservoir, $\mathcal{R}$. The micro-states of the system will be denoted by m_i. If I assume that the system is ergodic and all the micro-states corresponding to any fixed E and N are equally probable, then the probability associated with any state, say $p(m_{E,N})$ satisfies

$$p(m_{E,N}) \propto e^{\beta(E-\mu N)}, \tag{1}$$

where $\beta \equiv 1/(k_B T)$, T is the temperature and μ is the chemical potential of the reservoir.

The same probability distribution may be obtained if we take as starting point information theory [6]. The information we start with is the average energy and the average particle number, E and N, respectively. Then the probability distribution (1) is the least biased estimate possible on the given information [6]. From this point of view it has importance if the system is ergodic or not. For a macroscopic system the maximum of the probability distribution is sharply peaked around the average values, $\langle N \rangle$ and $\langle E \rangle$, so both particle number and internal energy have well-defined values.

Now let us assume that we can calculate (and measure) a macroscopic parameter, which I shall denote by X. The probability distribution over the micro-states is given by equation (1) and from this one can calculate the probability distribution over the parameter X:

$$P_x(X) = \sum_{i}^{X(m_i)=X} p(m_i). \tag{2}$$

If X is well defined, then $P_x(X)$ should have a sharp peak at $X = \langle X \rangle$. If $P_x(X)$ has two maxima, then the system undergoes a phase transition. In each of the phases, one maximum dominates and this fixes the value of X for that phase [2, 7] (say we have X_1 for phase 1 and X_2 for phase 2). If the total energy corresponding to phase 1, $E(X_1)$, is different from the total energy in phase 2, $E(X_2)$, then the phase transition is of order 1. Otherwise it is of higher order [7].

For a system of fermions, a parameter which is surprisingly interesting to analyse is the number of particles that occupy completely an energy interval (no holes left in this interval) starting at the bottom of the single-particle spectrum [2, 11, 12]—let us call this parameter N_0 and the energy interval $[0, \epsilon_0]$. In [2] I gave an example of an interacting system for which the probability distribution $P_n(N_0)$ forms, below a certain temperature, two competing maxima.

One maximum, which exists for any $T > 0$, is located at $N_0 = 0$ and the other appears at finite N_0. At transition temperature the maximum centred at $N_0 > 0$ equals the maximum existent at $N_0 = 0$ and a first-order phase transition occurs. Above the transition temperature $P_n(N_0)$ is maximum at $N_0 = 0$ and $\langle N_0 \rangle (\gtrsim 0)$ is microscopical. Below transition temperature $P_n(N_0)$ is maximum at $N_0 > 0$, so $\langle N_0 \rangle > 0$ is a macroscopic quantity. Due to the interaction, an energy gap is formed between the degenerate N_0 particles and the rest of the particles.

The same parameter may be analysed for a system of ideal fermions. Assume that the density of states (DOS) has the general form $\sigma(\epsilon) = K\epsilon^s$, where K and s are constants. Now I require that N_0 particles form a degenerate subsystem on the first N_0 energy levels, and the first hole in the spectrum appears at energy ϵ_0 (or energy level $N_0 + 1$—see [11] for details). Using again equation (2), I calculate $P_n(N_0)$. If $\mathcal{Z}$ is the partition function of the system, and $\mathcal{Z}_{N_0}$ is the number of configurations with the first hole appearing at $N_0 + 1$, then $P_n(N_0) = \mathcal{Z}_{N_0}/\mathcal{Z}$, where

$$\log \mathcal{Z}_{N_0} = \left[-\beta \left(K \frac{\epsilon_0^{s+2}}{s+2} - \epsilon_0 \right) + \beta\mu \left(K \frac{\epsilon_0^{s+1}}{s+1} - 1 \right) \right] + K \int_{\epsilon_0}^{\infty} d\epsilon \, \epsilon^s \log[1 + e^{-\beta(\epsilon-\mu)}]. \tag{3}$$

Since $\mathcal{Z}$ is a constant, the extrema of P_n are found by solving $d\mathcal{Z}_{N_0}/dN_0 = 0$ or equivalently [11],

$$\frac{d \log \mathcal{Z}_{N_0}}{d\epsilon_0} = -K\epsilon_0^s \left\{ \log[1 + e^{\beta(\epsilon_0-\mu)}] - \frac{\beta}{K\epsilon_0^s} \right\} = 0. \tag{4}$$

If $s > 0$, then $\log P_n$ has one and only one maximum at $N_0 > 0$, so for any macroscopic systems (i.e. large enough K) there will be a degenerate subsystem on the lowest energy levels at any temperature. If $s = 0$ (e.g. particles in a two-dimensional flat potential or in a one-dimensional harmonic potential) there is a transition temperature, $T_{c,2D}$, below which the maximum of $P(N_0)$ moves from $N_0 = 0$ to $N_0 > 0$, i.e. a degenerate gas forms. The degenerate gas may be put in correspondence with the the Bose–Einstein condensate in a gas of bosons with similar spectrum [2, 11–13] and for simplicity I shall call it the *Fermi condensate* or the degenerate subsystem. The most interesting case seems to be $s < 0$, when $\log P$ has either only one maximum, at $N_0 = 0$, or two maxima, at $N_0 = 0$ and $N_0 > 0$. As the temperature decreases, the second maximum increases and becomes bigger than the maximum at $N_0 = 0$.

2.1. Fermi condensation for constant density of states

For constant σ, in the (quasi)continuous limit ($\sigma k_B T \gg 1$), we have

$$\log \mathcal{Z}_{N_0} = \frac{-\beta\sigma\epsilon_0^2}{2} + \beta\mu \left(\sigma\epsilon_0 + \frac{\epsilon_0}{\mu} - 1 \right) + \sigma \int_{\epsilon_0}^{\infty} d\epsilon \log[1 + e^{-\beta(\epsilon-\mu)}]. \tag{5}$$

In such a case equation (4) has a solution if and only if $\log[1 + e^{-\beta\mu}] < (\sigma k_B T)^{-1}$. Therefore, as in [11], I define the condensation temperature $T_{c,F}$ by the equation

$$\log[1 + e^{-\beta_{c,F}\mu}] = (\sigma k_B T_{c,F})^{-1}. \tag{6}$$

Since $\sigma k_B T \gg 1$, then equation (6) implies that for $T \leqslant T_{c,F}$ we have $\mu/k_B T \gg 1$. Using the approximation $N \approx \sigma\mu$, valid for $\beta\mu \gg 1$ and equation (6) I get a simpler equation for $T_{c,F}$:

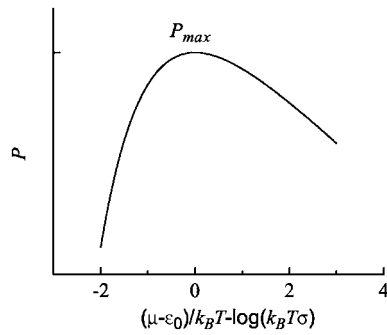$$N \approx \sigma k_B T_{c,F} \log(\sigma k_B T_{c,F}). \tag{7}$$

Figure 1. Probability distribution around the maximum value, of the number of particles in the condensate, as a function of $(\mu - \epsilon_0)/k_B T$, $(\mu - \epsilon_0)/k_B T = \sigma k_B T$. The absolute values of $P(\epsilon_0)$ are irrelevant here, so are omitted. The distribution is asymmetric, with $\langle N_0 \rangle < N_{0,\max}$.

For $T < T_{c,F}$ equation (4) becomes $\log[1 + e^{\beta(\epsilon_0 - \mu)}] = (\sigma k_B T)^{-1} (\ll 1)$ and its solution may be approximated by

$$\epsilon_{0,\max} = \mu - k_B T \log[\sigma k_B T]. \tag{8}$$

The particle number that is associated with $\epsilon_{0,\max}$ is $N_{0,\max} = \epsilon_{0,\max}\sigma = \sigma\mu - \sigma k_B T \log[\sigma k_B T]$. The distribution $P_n(N_0)$ is not symmetric (see figure 1) and $\langle N_0 \rangle < N_{0,\max}$ [22]. In the low-temperature limit $\langle N_0 \rangle$ converges to $N_{0,\max}$, but a closed general expression for $\langle N_0 \rangle$ is difficult to find.

3. Thermodynamic equivalence from the macroscopic point of view

As mentioned in the introduction, two gases are thermodynamically equivalent if they have the same canonical heat capacity C at any temperature and particle number. Integrating $(C/T)\,\mathrm{d}T$ from 0 to T, we obtain the entropy $S(T, N, \ldots)$ (the entropy might depend on other extensive parameters—like σ or V—which I do not specify explicitly), which is also the same for the two gases. Nevertheless, the entropy is usually defined as a function of $U, N, \ldots$, and if the two gases do not have the same $U(T)$ for any T, then the entropies as functions of the extensive variables are also different. Nevertheless, we can make the entropies coincide by translating $S(U, N, \ldots)$ along the U axis, for any N.

Let us take as example the Fermi and Bose gases of equal and constant σ. Under grandcanonical conditions, the entropy and internal energy of a Fermi gas have the expressions

$$S = -\sigma k_B^2 T [2Li_2(-e^{\beta\mu}) + \beta\mu \log(1 + e^{\beta\mu})] \tag{9}$$

and

$$U = -(k_B T)^2 \sigma Li_2(-e^{\beta\mu}), \tag{10}$$

respectively. Combining (9) and (10) I get

$$S = \frac{2U}{T} - \frac{\mu}{T}N \equiv \frac{U}{T} - \frac{\Omega_F}{T} - \frac{\mu}{T}N, \tag{11}$$

where $\Omega_F = -U$ is the grandcanonical potential of the gas. The average number of particles in the gas is

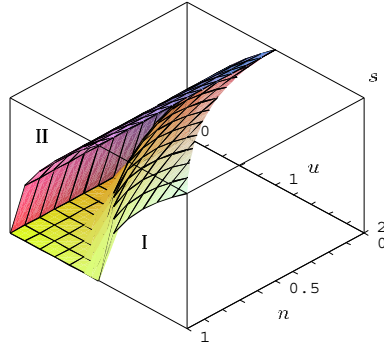$$\tilde{N} = \sigma\mu + \sigma k_B T \log[1 + e^{-\beta\mu}]. \tag{12}$$

Figure 2. Surface I: the entropy of a Fermi system, $s \equiv S/k_B\sigma$, as a function of $N \equiv N/\sigma$ and $u \equiv U/\sigma$. The range on the vertical axis is from 0 to $\pi\sqrt{2/3}$. Surface II is obtained from surface I by subtracting from the energy U, the ground state energy of the system, $U_{\text{g.s.}}(N) = N^2/2\sigma$.

(This figure is in colour only in the electronic version)

To work in the variables U and N we have to invert equations (10) and (12) and plug the expressions we obtain for T and μ into (9). Vice versa, from $S(U, N, \ldots)$, the temperature and the chemical potential are calculated as $T = (\partial S/\partial U)^{-1}$ and $-\mu/T = (\partial S/\partial N)^{-1}$, which can then be used to write $S = S(T, \mu, \ldots)$.

For our case, to obtain simple expressions for T, μ and S let us do the calculations in the low-temperature limit. In this limit $\beta\mu \gg 1$ and I can neglect $e^{-\beta\mu}$ from equation (12), retaining

$$N \approx \beta\mu. \tag{13}$$

On the other hand, using the expansion

$$Li_2(-e^{\beta\mu}) \approx -\frac{(\beta\mu)^2}{2}\left[1 + \frac{\pi^2}{3(\beta\mu)^2}\right] \tag{14}$$

and equation (13), U may be approximated as

$$U \approx \frac{N^2}{2\sigma}\left[1 + \frac{\pi^2}{3}\cdot\left(\frac{\sigma k_B T}{N}\right)^2\right]. \tag{15}$$

Eliminating $k_B T$ and $\beta\mu$ from equations (13) and (15) and plugging it into (9) I get

$$\frac{S}{k_B\sigma} \approx \pi\sqrt{\frac{2}{3}\cdot\left(\frac{U}{\sigma} - \frac{N^2}{2\sigma^2}\right)}. \tag{16}$$

The result (16) is plotted as surface I in figure 2.

I denote the zero-temperature energy of the Fermi gas by $U_0(N) \equiv N^2/2\sigma$ and I define the excitation energy, $U_B \equiv U - U_0(N)$. With these notations, I introduce $S_B(U_B, N) \equiv S(U_B + U_0(N), N)$, which in the low-temperature limit is

$$\frac{S_B}{k_B\sigma} \approx \pi\sqrt{\frac{2}{3}\cdot\frac{U_B}{\sigma}}. \tag{17}$$

Equation (17) is plotted as surface II in figure 2. The chemical potential of the gas B is related to the chemical potential of the Fermi gas by $\mu_B = \mu - dU_0/dN = \mu - \epsilon_F$.

Otherwise, a general expression for U_B may be obtained by using Landen's relation, $Li_2(-y) + Li_2[y/(y + 1)] = -\frac{1}{2}\log^2(1 + y)$ [1, 16]:

$$U = (k_BT)^2\sigma Li_2[(1 + e^{-\beta\mu})^{-1}] + \frac{(k_BT\sigma)^2}{2\sigma}\ln^2(1 + e^{\beta\mu})$$
$$= U_B + U_0(N),$$

where

$$U_B = (k_BT)^\sigma Li_2[(1 + e^{-\beta\mu})^{-1}] \tag{18}$$

and

$$U_0(N) = \frac{(k_BT\sigma)^2}{2\sigma}\ln^2(1 + e^{\beta\mu}) = \frac{N^2}{2\sigma}.$$

Applying Landen's relation to equation (9), I get

$$S = \frac{2U_B}{T} + \frac{N^2}{\sigma T} - \frac{\mu}{T}N$$
$$= \frac{2U_B}{T} - \frac{\mu_B}{T}N \equiv \frac{U_B}{T} - \frac{\Omega_B}{T} - \frac{\mu_B}{T}N, \tag{19}$$

where $\Omega_B = -U_B/T$ is the grandcanonical potential of the gas B [2].

The gas B, which has the zero-temperature energy, $U_{B,0}$, identically zero by construction, and the same heat capacity as the Fermi gas: $\partial S/\partial U = \partial S_B/\partial U_B = 1/T$ and $\partial U/\partial T = \partial U_B/\partial T$, is thermodynamically equivalent to the Fermi gas and therefore can only be the ideal Bose gas. By Landen's relations [1, 2, 8] we can rewrite U_B and N as

$$U_B \equiv \sigma(k_BT)^2 Li_2(e^{\beta\mu_B}) = \int_0^\infty \frac{\epsilon\sigma\,d\epsilon}{e^{\beta(\epsilon-\mu_B)} - 1} \tag{20}$$

and

$$N = -\sigma k_BT \log[1 - e^{\beta\mu_B}] = \int_0^\infty \frac{\sigma\,d\epsilon}{e^{\beta(\epsilon-\mu_B)} - 1} \tag{21}$$

(where $e^{-\beta\mu_B} = 1 + e^{-\beta\mu}$), which make the construction consistent. Note also that for the ideal gases μ_B is always negative.

4. Ideal canonical gases at low temperatures

Nevertheless, at very low temperatures, say below $T_{c,F}$, the macroscopic considerations from the previous section do no longer apply. Take for example equation (12) and calculate $\mu - \epsilon_F \equiv \mu_B$ in the limit $\beta\mu \gg 1$. We obtain

$$\mu_B \approx -k_BT\,e^{-N/\sigma k_BT} \tag{22}$$

from where, if we set, let us say $T = T_{c,F}/2$, the population of the ground state of the Bose system becomes

$$N_{0,B} = \frac{1}{e^{-\beta\mu_B} - 1} \approx (\sigma k_BT)^2 = N\frac{\sigma k_BT}{\log(\sigma k_BT)} \gg N, \tag{23}$$

which cannot be true [20]. A standard procedure to solve such a problem in the Bose system is to take the population of the ground state separately into account and write the total particle

number as

$$N = N_0 + \int_{\sigma^{-1}}^{\infty} \frac{\sigma \, d\epsilon}{e^{\beta(\epsilon - \mu_B)} - 1} = N_0 + \sigma k_B T \log[1 - e^{-\beta(\sigma^{-1} - \mu_B)}], \qquad (24)$$

with a smaller value of μ_B, i.e. $\mu_B < \mu - \epsilon_F < 0$. Since $N_{0,B} \approx (-\beta \mu_B)^{-1}$, then equation (23) implies

$$0 < (\mu - \epsilon_F)/\mu_B \ll 1. \qquad (25)$$

(Note that in the literature there are more exact ways to calculate the canonical population of the single-particle levels (see, for example, [13, 20]) but here I want only to show the procedure by which the thermodynamic equivalence between the Bose and the Fermi gases can be restored below the condensation temperature, so I consider only the leading order corrections.) Apparently, there is no way to accord the fermionic and the bosonic pictures of the gas. Equation (23) implies that if we translate the surface I (from figure 2) by making the transformation $S(U, N, \ldots) \to S(U_B, N, \ldots)$, we do not obtain the entropy of the Bose gas—at least we do not obtain it close to the N axis.

On the other hand, by the method outlined in [2, 12], which was called, for brevity, *exclusion statistics transformation* (EST), every distribution of fermions along the single-particle energy axis is transformed into a distribution of bosons and the N_0 fermions that form the Fermi condensate are mapped onto the bosons in the Bose condensate. For systems of constant DOS it is proved by EST that the Bose and the Fermi gases are equivalent at any temperature in any detail. Moreover, a Fermi grand-canonical probability distribution is transformed by EST into a Bose grand-canonical probability distribution (see section V.A of [12]). Therefore, since the Bose condensate can correspond only to the degenerate subsystem in the Fermi gas, this degenerate subsystem has to be taken into account separately in a canonical Fermi gas, especially at low temperatures. To prove this, the grand-canonical probability distribution of N_0 (equation (3)) was investigated in [12] and it was shown that it almost coincides with the Bose canonical probability distribution of the ground-state population. The small difference between these distributions is due to the total particle number fluctuation in the grand-canonical Fermi system. Therefore, in the canonical calculation, the expression for the total particle number (12) has to be corrected as

$$N = \langle N_0 \rangle + \int_{\langle \epsilon_0 \rangle + \sigma^{-1}}^{\infty} \frac{\sigma \, d\epsilon}{e^{\beta(\epsilon - \mu_c)} + 1} = \sigma \mu_c - 1 + \sigma k_B T \log \left[1 + e^{\beta(\langle \epsilon_0 \rangle + \sigma^{-1} - \mu_c)} \right]. \qquad (26)$$

This correction leads to a smaller value of the *canonical chemical potential*, μ_c, which restores the thermodynamical equivalence by satisfying the relation $\mu_B = \mu_c - \epsilon_F$. The asymptotic value of μ_c may be calculated using the canonical value of μ_B approximated in equation (24). Since the condensate starts to form when $\mu_B \approx -\sigma^{-1}$ (see, for example, [24]), well below the condensation temperature we can approximate $\exp[\beta(\sigma^{-1} - \mu_B)]$ by $\exp(\beta \sigma^{-1}) \approx 1 + \beta \sigma^{-1}$, which, if plugged back into (24) gives a simple expression for the asymptotic behaviour of μ_c at low temperatures:

$$\begin{aligned} \beta(\epsilon_F - \mu_c) = -\beta \mu_B &= [N - \sigma k_B T \log(\sigma k_B T)]^{-1} \\ &\approx \frac{1}{N} + \frac{\sigma k_B T \log(\sigma k_B T)}{N^2}. \end{aligned} \qquad (27)$$

If we drop the $1/N$ term from the last line above, which comes from the fact that the Fermi condensate has to be separated by a hole from the rest of the gas, then we obtain an (almost) parabolic dependence on temperature of the chemical potential: $\mu_c = \epsilon_F - (k_B T/\epsilon_F)^2 \cdot \log(\sigma k_B T)/\sigma$, while the textbook result for this is $\mu = \epsilon_F - k_B T \exp(N/\sigma k_B T)$ (22).

5. Conclusions

I discussed the effect of fermionic condensation—which is the apparition of a degenerate subsystem at the bottom of the single-particle spectrum—in a system of constant density of states. This leads to a correction in the calculation of the chemical potential in the canonical ensemble at low temperatures (see equation (27)) and of the grand-canonical occupation probability of the single-particle levels.

Shifts of the chemical potential in finite Fermi gases due to finite size effects have never been reported before. This shift corrects the textbook expression for the low-temperature limit of the chemical potential.

By applying the exclusion statistics transformation to the Fermi system, one obtains a (thermodynamically equivalent [2]) Bose system. If the Fermi system is condensed, the degenerate subsystem is mapped onto the Bose–Einstein condensate and for this reason the name *Fermi condensate* was used. The Fermi condensate fluctuates and the values of these fluctuations are simply given by the condensate fluctuations of the equivalent Bose system [13, 18].

The results above may also be interpreted as a finite size correction of Jaynes' theory [6]. According to this theory, the probability that a microscopic configuration is realized has the form (1), which represents the least biased estimate given that the average number of particles in the system is N and the average energy is U. Distribution (1), applied to an ideal gas of fermions, leads to the Fermi grand-canonical distribution. On the other hand, the bosonic distribution of the equivalent Bose gas is the least biased estimate, given the average *excitation energy U_B* and particle number N. As shown in this paper, the two distributions *do not map onto each other over the whole spectrum* and they have to be corrected if the temperature is lower than the condensation temperature. In other words, Jaynes' probability distribution is sensitive at low temperatures to the finite, fixed value of N in the canonical ensemble. In [12] it is proved that the situation is even more dramatic when the DOS is not constant.

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