

# Thermodynamic Limit of the Free Electron Gas on a Circle

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We show that for the ground state of a one-dimensional free electron gas on a circle the analytic expression for the canonical ensemble partition function can be easily derived from the density matrix by assuming that the thermodynamic limit coincides with the limit of the eigenfunction expansion of the kinetic energy. This approximation fails to give the finite temperature partition function because those two limits cannot be chosen as coincident.

*Keywords:* Thermodynamic limit; free electron gas; circle; density matrix; canonical ensemble.

## 1. Introduction

In statistical physics textbooks, like for example the Feynman (1972) “Statistical Mechanics: A Set of Lectures”<sup>1</sup> Sec. 2.8, the derivation of an analytic expression for the partition function of the free fermion or boson gas is accomplished choosing to work in the grand canonical ensemble. In this brief paper, we show the difficulties one goes through if he insists in choosing to work in the canonical ensemble instead. For definiteness, we will consider polarized fermions.

Some recent studies on the electron gas or *the jellium* are about two-dimensional systems<sup>2–9</sup> or three-dimensional ones.<sup>3,10–15</sup> Here, we will just consider an ideal electron gas in one dimension at a finite absolute temperature  $T$ .

The main actor of our problem is the thermal density operator  $\hat{\rho} = e^{-\beta\hat{H}}$  where  $\hat{H}$  is the Hamiltonian operator and  $\beta = 1/k_B T$  with  $k_B$  Boltzmann’s constant. We will only work in position representation so that  $\rho(\mathbf{r}, \mathbf{r}'; \beta) = \langle \mathbf{r} | e^{-\beta\hat{H}} | \mathbf{r}' \rangle$ .

## 2. A Simple Derivation

Consider first one single free electron of mass  $m$  in a one-dimensional box of width  $L$  with periodic boundary conditions, which is the same as saying that the electron lives in a circle. Its wave function  $\psi(x)$  is such that  $\psi(x + L) = \psi(x)$  and satisfies Schrödinger’s equation, namely

$$-\lambda \frac{\partial^2 \psi(x)}{\partial x^2} = E \psi(x), \quad (2.1)$$

where  $\lambda = \hbar^2/(2m)$ .

The solution of Eq. (2.1) is as follows<sup>16</sup>:

$$E_n = \lambda \left( \frac{2\pi}{L} \right)^2 n^2, \quad n = 0, 1, 2, 3, \dots \quad (2.2)$$

$$\psi_n(x) = \frac{1}{\sqrt{L}} \exp\left(i \frac{2\pi}{L} n x\right), \quad 0 < x < L, \quad (2.3)$$

where  $E_n$  are the eigenvalues and  $\psi_n$  the normalized eigenvectors.

At an inverse temperature  $\beta = 1/k_B T$ , the exact density matrix

$$\rho_1(x, y; \beta) = \sum_{n=-\infty}^{\infty} \psi_n^*(x) \psi_n(y) \exp(-\beta E_n)$$

for one of those fermions in periodic boundary conditions is

$$\begin{aligned} \rho_1(x, y; \beta) &= \frac{1}{L} \theta_3 \left( \frac{\pi}{L} (x - y), \exp \left( -\beta \lambda \left( \frac{2\pi}{L} \right)^2 \right) \right) \\ &= \lim_{q \rightarrow \infty} \frac{1}{L} \sum_{n=-q}^q \exp \left( -\beta \lambda \left( \frac{2\pi}{L} \right)^2 n^2 \right) \\ &\quad \times \exp \left( -i \frac{2\pi}{L} n (x - y) \right) \\ &= \lim_{q \rightarrow \infty} k_q(x, y; \beta), \end{aligned} \quad (2.4)$$

where  $\theta_3(z, q)$  is a theta function (see Abramowitz and Stegun,<sup>17</sup> Chap. 16, for its properties).

Consider now  $N = 2p + 1$  (with  $p = 0, 1, 2, 3, \dots$ ) free polarized fermions on a circle of circumference  $L$ . Usually for an electron gas, it is more common to introduce Hartree's units where lengths are given in units of  $a = L/N = 1/\rho$ , with  $\rho$  the density of the gas, energies are given in Rydbergs  $\hbar^2/(2ma_0^2)$ , where  $a_0 = \hbar^2/(me^2)$ , with  $e$  the electron charge, is Bohr's radius. And the kinetic energy scales like  $1/r_s^2$  with  $r_s = a/a_0$ . But since here we are dealing with a non interacting gas, we prefer not to use these conventions which would only make formulas less intuitive and pedagogic.

The density matrix of the  $N$  fermions is now<sup>1,16</sup>

$$\begin{aligned} \rho_N(\mathbf{x}, \mathbf{y}; \beta) &= \frac{1}{N!} \det \{ \rho_1(x_i, y_j; \beta) \}_{i,j=1}^N \\ &= \lim_{q \rightarrow \infty} \frac{1}{N!} \det \{ k_q(x_i, y_j; \beta) \}_{i,j=1}^N \\ &= \lim_{q \rightarrow \infty} K_q(\mathbf{x}, \mathbf{y}; \beta), \end{aligned} \quad (2.5)$$

where  $\mathbf{x} = (x_1, x_2, \dots, x_N)$ ,  $\mathbf{y} = (y_1, y_2, \dots, y_N)$ , and  $y_i, x_j$  are the initial and final positions of the  $N$  fermions.

Note that because of Pauli's principle<sup>16</sup> (see Appendix A)

$$K_q = 0 \quad \text{when } q < p. \quad (2.6)$$

For the particular case  $q = p$  there is a simple expression for  $K_q$ , namely,

$$\begin{aligned} K_p(\mathbf{x}, \mathbf{y}; \beta) &= \frac{1}{N!} \frac{2^{N(N-1)}}{L^N} \exp \left( -2\beta \lambda \left( \frac{2\pi}{L} \right)^2 \sum_{n=1}^p n^2 \right) \\ &\quad \times \prod_{1 \leq i < j \leq N} \sin \left( \frac{\pi}{L} (x_i - x_j) \right) \sin \left( \frac{\pi}{L} (y_i - y_j) \right). \end{aligned} \quad (2.7)$$

This expression is the exact density matrix of the ground state (when  $\beta \rightarrow \infty$ ) of the  $N$  fermions.

For example, let's find the partition function  $Z(\beta) = \text{tr}(\hat{\rho}_N) = \int \rho_N(\mathbf{x}, \mathbf{x}; \beta) d\mathbf{x}$  of the fermion system in the thermodynamic limit. We need to calculate the trace  $Z_p(\beta)$  of  $K_p(\mathbf{x}, \mathbf{y}; \beta)$  and then take  $p$  to infinity

$$\begin{aligned} Z_p(\beta) &= \int_{-L/2}^{L/2} dx_1 \cdots \int_{-L/2}^{L/2} dx_N K_p(\mathbf{x}, \mathbf{x}; \beta) \\ &= \exp \left( -2\beta \lambda \left( \frac{2\pi}{L} \right)^2 \sum_{n=1}^p n^2 \right) \frac{1}{N!} \frac{2^{N(N-1)}}{(2\pi)^N} I_N, \end{aligned} \quad (2.8)$$

where

$$\begin{aligned} I_N &= \int_{-\pi}^{\pi} d\theta_1 \cdots \int_{-\pi}^{\pi} d\theta_N \prod_{1 \leq i < j \leq N} \sin^2 \left( \frac{\theta_i - \theta_j}{2} \right) \\ &= N! \frac{(2\pi)^N}{2^{N(N-1)}}. \end{aligned} \quad (2.9)$$

So, we get

$$Z_p(\beta) = \exp \left( -2\beta \lambda \left( \frac{2\pi}{L} \right)^2 \sum_{n=1}^p n^2 \right). \quad (2.10)$$

Or for the Helmholtz free energy,  $F = -\ln Z/\beta$ ,

$$\begin{aligned} F_p(\beta) &= 2\lambda \left( \frac{2\pi}{L} \right)^2 \sum_{n=1}^p n^2 \\ &= \frac{\pi^2}{3} \rho^2 \lambda \frac{N^2 - 1}{N}. \end{aligned} \quad (2.11)$$

And in the thermodynamic limit,

$$f(\beta) = \lim_{p \rightarrow \infty} \frac{F_p(\beta)}{N} = \frac{\pi^2}{3} \rho^2 \lambda. \quad (2.12)$$

As expected the free energy is independent of temperature in the thermodynamic limit. Moreover, we found the expected results for the ground state

energy

$$\begin{aligned}
 E_0 &= \lambda L \int_{-k_F}^{k_F} k^2 \frac{dk}{2\pi} \\
 &= \left( \frac{L}{2\pi} \right) \frac{2}{3} \lambda k_F^3 \\
 &= N \left( \frac{\lambda \rho^2 \pi^2}{3} \right), \tag{2.13}
 \end{aligned}$$

where the Fermi wave vector is  $k_F = \pi\rho$ .

But we see from Eq. (2.5) that in the thermodynamic limit (i.e.  $p \rightarrow \infty$  and  $\rho = N/L$  constant) it fails to give the exact density matrix of the fermions at finite inverse temperature  $\beta$  for which it is necessary to relax the constraint  $q = p$  and respect the order of the two limits, first the one over  $q$  and only later the one over  $p$ .

### 3. Conclusions

When writing the canonical partition function of a free electron gas on a circle in the thermodynamic limit one has to deal with two kinds of limits: The limit of the eigenfunction expansion of the kinetic energy and the thermodynamic limit. In this brief paper, we showed that if one takes the two limits as coincident then necessarily falls in the ground state case, the  $\beta \rightarrow \infty$  limit. In this case, in fact, the zero temperature limit permits to take those two limits as the same. But in order to find the correct finite temperature case, it is necessary to take those two limits independently in the correct order.

## Appendix A

### A Determinantal Identity

Given three functions of two variables,  $K(x, y)$ ,  $L(x, y)$  and  $M(x, y)$  such that

$$K(x, y) = \sum_{n=-\infty}^{\infty} L(x, n)M(n, y). \tag{A.1}$$

Take the following product:

$$\begin{aligned}
 &K(x_1, y_{\pi 1})K(x_2, y_{\pi 2}) \cdots K(x_n, y_{\pi n}) \\
 &= \sum_{k_1, k_2, \dots, k_n} [L(x_1, k_1)L(x_2, k_2) \cdots L(x_n, k_n)] \\
 &\quad \times [M(k_1, y_{\pi 1})M(k_2, y_{\pi 2}) \cdots M(k_n, y_{\pi n})]. \tag{A.2}
 \end{aligned}$$

Summing appropriately with respect to all permutations, we obtain

$$\begin{aligned}
 &\det\{K(x_i, y_j)\}_{i,j=1}^n \\
 &= \sum_{k_1, k_2, \dots, k_n} L(x_1, k_1)L(x_2, k_2) \cdots L(x_n, k_n) \\
 &\quad \times \det\{M(k_i, y_j)\}_{i,j=1}^n. \tag{A.3}
 \end{aligned}$$

The region of summation can be decomposed in nonoverlapping regions  $\Delta_\nu$  characterized by the inequalities  $k_{\nu 1} < k_{\nu 2} < \cdots < k_{\nu n}$ , where  $\nu$  is an arbitrary permutation of the set  $(1, 2, \dots, n)$  into itself.

Transforming the region  $\Delta_\nu$  by the change of variable  $k_{\nu i} \rightarrow k_i$  ( $i = 1, 2, \dots, n$ ) and collecting the resulting sums, we obtain, for the right-hand side of (A.3)

$$\begin{aligned}
 &\sum_{k_1 < k_2 < \dots < k_n} \sum_{\nu} (-)^{|\nu|} L(x_1, k_{\nu-1 1})L(x_2, k_{\nu-1 2}) \\
 &\quad \cdots L(x_n, k_{\nu-1 n}) \det\{M(k_i, y_j)\}_{i,j=1}^n, \tag{A.4}
 \end{aligned}$$

where the signature  $(-)^{|\nu|}$  in each term appears as a consequence of rearranging the rows of  $\det M$ .

So, we derived the following composition formula<sup>a</sup>:

$$\begin{aligned}
 &\det\{K(x_i, y_j)\}_{i,j=1}^n \\
 &= \sum_{k_1 < k_2 < \dots < k_n} \det\{L(x_i, k_j)\}_{i,j=1}^n \\
 &\quad \times \det\{M(k_i, y_j)\}_{i,j=1}^n. \tag{A.5}
 \end{aligned}$$

Applied to the function  $k_q$  defined in (2.4) as

$$k_q(\theta, \phi) = \sum_{n=-q}^q \mu_n e^{in\theta} e^{-in\phi}, \tag{A.6}$$

we see that for  $q \geq (N-1)/2$

$$\begin{aligned}
 &\det\{k_q(\theta_i, \phi_j)\}_{i,j=1}^N \\
 &= \mu_0 \prod_{n=1}^q |\mu_n|^2 \sum_{-q \leq k_1 < k_2 < \dots < k_n \leq q} \det\{e^{ik_j \theta_i}\}_{i,j=1}^N \\
 &\quad \times \det\{e^{-ik_i \phi_j}\}_{i,j=1}^N. \tag{A.7}
 \end{aligned}$$

So when  $q = (N-1)/2$  the sum has only one term which is given by Eq. (2.7). And for  $q < (N-1)/2$ ,  $\det\{k_q\} = 0$ .

<sup>a</sup>Which holds also after replacing the sums with integrals.

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**Riccardo Fantoni** was born in Livorno on the 30 August 1970, lived in Pisa until 1995 where graduated “cum Laude” in the department of Physics of the University. Then moved as a graduate student to the University of Illinois at Urbana/Champaign until 2000 working as a Teaching and Research Assistant and in 1997 got a Master in Physics. Moved to Trieste and in 2004 got a Ph.D. in Physics. From 2005 to 2008 worked at the Chemical Physics department of the University “Ca’ Foscari” of Venice as a postdoctoral research and teaching fellow. From 2009 to 2012 worked at the National Institute for Theoretical Physics of the University of Stellenbosch as a postdoctoral research fellow. In 2018 got a full professorship as a mathematics teacher in the secondary Italian school of second degree. In 2019 won the habilitation as an associate professor in theoretical physics of matter in the Italian university system.

Aim of his research is to develop analytical and computational methods for condensed and soft matter starting from the fundamental many-body equations. Apart from the few analytically exactly solvable models our principal instruments, guided by the various sum-rules, are Integral Equation Theory, Density Functional Theory, Thermodynamic Perturbation Theory, Association Theory, and Monte Carlo simulations which can find exact properties of many-body systems. We are combining these approaches to create new methods and to test the accuracy of calculations on materials. Current studied materials include colloidal suspensions, ionic liquids, polymer mixtures, the electron fluid, the polaron, and boson fluids (like  $^4\text{He}$ ,  $^4\text{He-H}_2$  mixtures, ...). We investigate the structure and thermodynamic properties of the materials including their phase transitions like the gas-liquid-(glass)-solid first order ones and the superfluid-superconducting second order ones, the percolation threshold, the clustering, the localization, the demixing, the polydispersity, and surface properties. Lately he started working on Euclidean relativistic covariant and ultralocal quantum scalar field theories through Path integral Monte Carlo of lattice field theory subject to different kinds of quantization procedures.