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Partition functions for many-particle systems

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The well-known cumulant-summation formula is applied to the low-temperature calculation of the quantum-mechanical partition functions for many-particle systems. The motivation for this method is to be able to deal with many-particle states directly and avoid the usual starting point of independent single-particle states. The test case chosen for this method was the calculation of the canonical partition function and the grand-canonical partition function for the degenerate free-electron gas. The result is that the expected equivalence of the canonical and grand-canonical ensembles is not found at low temperatures. The role of few-particle fluctuations in the grand-canonical ensemble is shown to be extremely important to the thermal properties of the degenerate free-electron gas and in the difference between the ensembles.

I. INTRODUCTION

This paper will present an application of the cumulant formula[1] for the exponentiation of a series, to the calculation of the low-temperature quantum-mechanical partition functions of degenerate many-electron systems. The initial motivation behind this application was to provide a possible approximation for the partition function in the grand-canonical ensemble that would not require the usual starting assumption of independent single-particle states. As a test for this methodology, it was decided to calculate both the canonical and grand-canonical partition functions of the degenerate free-electron gas, for which the grand-canonical partition function is well known. The apparent absence of canonical ensemble calculations is quite natural, given the difficulty in counting states and the well-known "proof" in the standard quantum statistical mechanics literature[2] on the equivalence of the two partition functions.

The initial expectation of this study was that for large particle number N, the canonical partition function Q_N should be the dominant term in the expression for the grand-canonical partition function $\mathcal{Z}$ when the chemical potential μ has been set so that the average number of particles is N. Furthermore, under these circumstances, the heat capacity calculated using Q_N and $\mathcal{Z}$ should be the same.

It was with great surprise that we found that the heat capacity derived from the cumulant formula for the canonical ensemble was not extensive, and did not agree with the linear T temperature dependence found in the grand-canonical ensemble and experiment.

This finding led to a number of inquiries about what could be wrong with the method of evaluation. A first question involved whether the evaluations were being conducted in the thermodynamic limit. Accordingly, all expressions were evaluated using a density of states per particle ρ, so that all factors of the number of particles N could be explicitly displayed. It will be seen below in the evaluation of $\mathcal{Z}$ that cancellations between terms involving powers of N are essential for convergence of the cumulant series to the grand-canonical partition function.

A second question arose about the convergence of the cumulant series. The convergence for the grand-canonical ensemble, exhibited below, insures that the cumulant series must converge for the canonical ensemble. Further, discussion below will indicate that the cumulant series can be more quickly convergent than the direct partition function series itself.

A third question about the canonical ensemble results, reported below, related to Fermi surface effects. All of these effects were proportional to $N^{2/3}$ and were negligible in the thermodynamic limit.

The discrepancy between Q_N and $\mathcal{Z}$ and the quick convergence of the cumulant approximation to $\mathcal{Z}$ forces a critical examination of the proofs in the statistical literature[3] that the two ensembles are the same.

As will be discussed below, these proofs are based on an assumption, without demonstration, that the dominant term in $\mathcal{Z}$ is best represented by Q_N and not by a collection of terms for some small integer m,

$$\exp(\Theta_m) = \sum_{r=-m}^{+m} Q_{N+r} \exp[\beta\mu(N+r)], \tag{1.1}$$

as is found in this study.

The essential difference, to be seen below, between the canonical and grand-canonical ensembles is that, in the canonical ensemble, the only allowed excitations are equal numbers of particles and holes. Only excitations with these restrictions maintain a fixed particle number. The simplest excitation will thus be a single-particle-hole pair, and these two independent excitations give rise to a T^2 behavior at low temperatures.[5] In contrast, for the grand-canonical ensemble, excitations representing changes in the number of particles allow the simplest excitations to be an additional particle above the filled Fermi sea, or a single hole in the filled Fermi sea. Each of these excitations, representing a single quasiparticle, gives rise to the expected linear T dependence at low temperatures. The additional technical details behind this simple picture will be presented below.

Quite apart from the surprising discrepancy between the ensembles, the success of the cumulant-summation formula in recovering the grand-canonical ensemble offers a potentially useful tool for the study of interacting many-particle systems.

The paper will be organized in the following manner. In Sec. II the cumulant method and the definitions of the two partition functions will be reviewed. The free-electron grand-canonical partition function will be calculated in two different fashions using the standard products of independent single-particle states as a starting point. The elements of the standard "proof" of ensemble equivalence will also be reviewed with an intent to illustrate how it could be altered.

In Sec. III, the calculation of the simplest approximation for the canonical partition function is carried out using the low-temperature cumulant formula. It will be adequate here to demonstrate that the derived exponential power in the canonical partition function is not extensive, and the temperature dependence at low temperatures of this simplest approximation is not in agreement with the grand-canonical partition function calculated in Sec. II. This discrepancy will be enough to make the first point of the paper and a complete calculation will not be given here.

In Sec. IV the cumulant method will be carried out to generate an approximation to the grand-canonical partition function for a system with a thermal expectation value of N electrons. In this calculation, for simplicity, it will be assumed that the one electron density of states per particle is constant. This assumption is not essential and could be lifted with significant additional labor.

The final section will briefly review some of the consequences of these results. Details of the cumulant calculations are included in the Appendix.

II. THE CUMULANT FORMULA

There have been a large number of applications of the concept of the cumulant.[4,6] Its major use has been in the field of statistics, but there have also been a number of applications in statistical mechanics.[7] Most of the applications have been made in classical statistical mechanics and in the study of the interacting gas.[8] Kubo[4] has written a classic paper showing a number of applications of the cumulant formula. Most previous applications of the cumulant formula led to expansions that were valid in the high-temperature regime. In this paper, the cumulant formula is used for low temperatures.

For the application of this paper the cumulant expansion can be regarded as a rearrangement theorem for a sum which closely resembles the expansion of an exponential, except that the terms t_n are not products of the argument of the exponential. Let us consider a series of the form

$$\exp(\Theta) = 1 + \sum_{n=1}^{\infty} \frac{t_n}{n!}, \tag{2.1}$$

where the terms t_n are not simple powers of some variable to the nth power. In our application t_1 is extensive (thermodynamically) and each other term t_n has dominant terms of order N^n. The rearrangement of this series to find Θ, which is the variable whose powers give the usual series expansion for the exponential, yields the following cumulant sum:

$$\Theta = \sum_{n=1}^{\infty} \frac{\kappa_n}{n!}, \tag{2.2}$$

where the κ_n are given by

$$\kappa_1 = t_1, \tag{2.3}$$

$$\kappa_2 = t_2 - t_1^2, \tag{2.4}$$

$$\kappa_3 = t_3 - 3t_2t_1 + 2t_1^3, \tag{2.5}$$

$$\kappa_4 = t_4 - 4t_3t_1 + 12t_2t_1^2 - 3t_2^2 - 6t_1^4, \tag{2.6}$$

$$\kappa_5 = t_5 - 5t_4t_1 - 10t_2t_3 + 20t_1^2t_3 + 30t_1t_2^2 - 60t_1^3t_2 + 24t_1^5. \tag{2.7}$$

Determination of the rth cumulant uses all the t_n up to r in the original series. A listing of the first few cumulants can be found in several handbooks[1] and a formula for the general cumulant is given by Mattis.[9]

If the series of κ's are quickly converging, finite sums have the potential of providing good approximations for the partition functions of interacting systems. In those systems the t_n will correspond roughly to the sum of terms with n excitations present.[10]

The partition function Q_N for the canonical ensemble for a Hamiltonian H in contact with an energy reservoir with temperature β^{-1} is defined as

$$Q_N = \mathrm{Tr}_N(e^{-\beta H}), \tag{2.8}$$

where the trace is taken over states with N particles.

The grand partition function $\mathcal{Z}$ is defined for a system that is in contact with a particle reservoir at chemical potential μ, which allows the exchange of particles and energy with the system. For systems described by the grand-canonical ensemble the number of particles for the system is not definite, but may fluctuate. The average number of particles $\langle N \rangle$ in the system is determined by the chemical potential. The grand partition function is defined as

$$\mathcal{Z} = \sum_{N=1}^{\infty} Q_N e^{\beta\mu N}. \tag{2.9}$$

From the definition of the grand-canonical partition function it is straightforward to derive the following useful formulas for the average energy $U = \langle E \rangle$ and the average number of particles $\langle N \rangle$:

$$U = \mu\langle N\rangle - \left(\frac{\partial \ln \mathcal{Z}}{\partial\beta}\right)_{\mu}, \tag{2.10}$$

$$\beta\langle N\rangle = \left(\frac{\partial \ln \mathcal{Z}}{\partial\mu}\right)_{\beta}, \tag{2.11}$$

where the subscripts indicate the variable held constant in the partial derivative.

From the early literature,[11] the grand-canonical partition function for the free-electron gas has been calculated by using the product theorem of statistical mechanics, which states that the partition function representing two independent subsystems is the product of the partition functions of the systems. For the grand partition function of a free-electron gas with one-electron energies of $\epsilon_{\mathbf{k}s}$ we may write

$$\mathcal{Z} = \prod_{\mathbf{k},s}\{1 + \exp[-\beta(\epsilon_{\mathbf{k}s} - \mu)]\}. \tag{2.12}$$

Applying Eqs. (2.10) and (2.11) to this product yields the standard definition for the energy and average particle number:

$$U = \sum_{\mathbf{k},s}\epsilon_{\mathbf{k}s} f(\epsilon_{\mathbf{k},s}) = \int g(\epsilon)\epsilon f(\epsilon)d\epsilon, \tag{2.13}$$

$$\langle N\rangle = \sum_{\mathbf{k},s} f(\epsilon_{\mathbf{k}s}) = \int g(\epsilon) f(\epsilon)d\epsilon, \tag{2.14}$$

where $f(\epsilon)$ is the Fermi function and $g(\epsilon)$ is the one-electron density of states for both spin states.

The standard procedure[3] is to take these two equations and carry out an integration by parts yielding an integral of $g(\epsilon)$ against the derivative of the Fermi function. At low temperatures this derivative is so sharply peaked at the chemical potential μ that the density of states can be expanded in a Taylor series about μ. The resulting integrals of powers of the energy with the sharply peaked factor lead to a (usually) asymptotic power series in temperature.

Using these series and calculating the heat capacity at constant particle number and constant volume gives

$$C_{\langle N\rangle} = \left(\frac{\partial U}{\partial T}\right)_{\langle N\rangle} = \gamma T = \left(\frac{\pi^2}{3} g(\mu) k_B^2\right) T, \tag{2.15}$$

where k_B is the Boltzmann constant. This calculation is complicated, but straightforward.

A simpler calculation can be obtained by first calculating the grand-canonical partition function directly from Eq. (2.12). The first step is to seek the logarithm of $\mathcal{Z}$, converting the products to sums and integrals over the density of states $g(\epsilon)$. By separating the integrals into two types, particle excitations $(\epsilon - \mu) > 0$ and hole excitations $(\epsilon - \mu) < 0$, one obtains integrals of $g(\epsilon)$ multiplied by $\ln(1 + X)$, where $X = \exp[\pm\beta(\epsilon - \mu)]$ which is small in either regime. A useful asymptotic expansion can be obtained from these integrals by first expanding the logarithms in a series expansion for small X and then also expanding the density of states in a Taylor series in $(\epsilon - \mu)$ and carrying out the resulting integrals of powers of $(\epsilon - \mu)$ and exponentials. The resulting expression for the grand partition function is

$$\ln(\mathcal{Z}) = -\beta[E(\mu) - \mu\langle N(\mu)\rangle] + 2\sum_{r=0}^{\infty}\frac{g^{[2r]}(\mu)\eta_r}{\beta^{2r+1}}, \tag{2.16}$$

where $g^{[n]}(\mu)$ is the nth derivative of the density of states evaluated at the chemical potential and η_r is defined as

$$\eta_r = \sum_{l=1}^{\infty}\frac{(-1)^{l+1}}{l^{2r+2}}, \tag{2.17}$$

and where

$$E(\mu) = \int_{\epsilon_0}^{\mu}\epsilon g(\epsilon)d\epsilon, \tag{2.18}$$

$$N(\mu) = \int_{\epsilon_0}^{\mu} g(\epsilon)d\epsilon. \tag{2.19}$$

Here ϵ_0 is the energy at the bottom of the band.

Using Eqs. (2.10) and (2.11) it is easy to derive the following expression for the energy:

$$U = E(\mu) + 2\sum_{r=0}^{\infty}\frac{[g^{[2r]}(\mu) + \mu g^{[2r+1]}(\mu)]\eta_r}{\beta^{2r+2}}, \tag{2.20}$$

and for the average number of particles,

$$\langle N\rangle = N(\mu) + 2\sum_{r=0}^{\infty}\frac{g^{[2r+1]}(\mu)\eta_r}{\beta^{2r+2}}. \tag{2.21}$$

For use in our later discussion it is appropriate to note that the heat capacity at constant chemical potential can be obtained easily from Eq. (2.20),

$$C_\mu = 2k\sum_{r=0}^{\infty}(2r+2)[g^{[2r]}(\mu) + \mu g^{[2r+1]}(\mu)]\eta_r(kT)^{2r+1}. \tag{2.22}$$

The heat capacity at constant particle number, Eq. (2.15), and corrections may be obtained easily from these equations by first determining the temperature derivative of the chemical potential so that $\langle N\rangle$ is constant in temperature.

It is currently standard practice to use $C_{\langle N\rangle}$ for interpreting experiments instead of C_μ. This practice is based on the standard argument in statistical mechanics that the canonical partition function is essentially the same as the grand-canonical partition function for large systems and that experiment must necessarily correspond most closely to the condition represented by the canonical ensemble where N is fixed and equal to $\langle N\rangle$.

Let us now reexamine this argument.[3] The key step in the argument is the unverified assumption that the dominant term in the grand-canonical partition function is $Q_N \exp(\beta\mu N)$, where for simplicity we write $N = \langle N\rangle$ for the average particle number. Because the Helmholtz free energy is extensive, this dominant term can be written in the form $\exp[V\phi(\beta, \frac{V}{N})]$ where ϕ is intensive with respect to the volume V and/or particle number N. Two rather weak inequalities are applied at this point to bound $\mathcal{Z}$. The first inequality simply states that the whole series must be larger than the single dominant term. The second inequality is chosen to dominate $\mathcal{Z}$. It is argued that for some large number of particles N_0 in the volume V the interactions raise the energy so much that Q_{N_0+r} is as small as desired. In this case one can argue that $\mathcal{Z}$ must be smaller than N_0 times the dominant term. It is further argued that N_0 must be proportional to the volume, $N_0 = aV$. These arguments can be combined to yield

$$\exp(V\phi) < \mathcal{Z} < aV\exp(V\phi). \tag{2.23}$$

Taking the logarithm and dividing by V gives

$$\phi < \ln(\mathcal{Z})/V < \phi + \ln(aV)/V. \tag{2.24}$$

As the volume becomes very large, the second term on the right side of the equality goes to zero and $\mathcal{Z}$ is approximated well by $\exp(V\phi)$.

The possibility that is ignored in this general argument is that there are systems where the dominant term in $\mathcal{Z}$ is represented by combinations of terms involving small fluctuations in particle number and that this sum dominates the simple Q_N contribution.

In the case for the grand-canonical partition function of the free-electron gas we will find below that the dominant collection of terms for small m

$$\exp(\Theta_m) = \sum_{r=-m}^{+m} Q_{N+r}\exp[\beta\mu(N+r)] \tag{2.25}$$

gives rise to an extensive Θ_m which converges to a Θ as $m \to \infty$, and which dominates the Helmholtz Free energy for N particles obtained from the canonical ensemble.

In Sec. IV we will see that the cumulant formula applied to $m = 5$ recovers the grand-canonical result to within about 2% at low temperatures.

The "standard" proof reviewed above used an inequality to show the equality of $\ln(\mathcal{Z})$ and its dominant terms in the thermodynamic limit. The cumulant formulas used in this study represent series for which each term t_n (or κ_n) is already evaluated in the thermodynamic limit. The question of convergence then becomes the usual criterion for the limit of partial sums of the series. A consideration of these limits indicates that the cumulant series κ_n can be more quickly convergent than the sum of the t_n. If T_N is the partial sum of the series of the t_n terms and if $\mathcal{Z}$ is the sum, then the series converges if for large enough N we have $|T_N - \mathcal{Z}| < \varepsilon$. If K_N is the corresponding partial sum of the cumulant series we also have that $|K_N - \ln(\mathcal{Z})| < \varepsilon/\mathcal{Z}$. This means that approximations determined by the cumulant series can be more strongly convergent to the partition function if $\mathcal{Z}$ is large.

For the low temperatures of interest here, the temperature dependence of the first cumulant κ_1 dominates the partition function. Higher-order κ_n give either corrections to the coefficient of the temperature dependence of κ_1 or contribute higher powers of temperature. When we examine the canonical ensemble below, we will explicitly evaluate only κ_1 and κ_2.

In the canonical ensemble, because of the restriction that the particle number is fixed, the lowest-energy excitations must be pairs of particle excitations and hole excitations. It is not possible in the canonical ensemble to have excitations with only a single particle and the filled Fermi sea or a single hole with the filled Fermi sea, since these would represent a change in the number of particles. Yet single-particle or hole excitations will always give low-temperature contributions to the partition function that are larger than the particle-hole pairs. In the calculations to follow this will manifest itself in a temperature dependence of β^{-1} for the single-particle or hole excitations and a temperature dependence of β^{-2} for the particle-hole pairs. It is the fact that the canonical ensemble only allows low-lying excitations made up of particle-hole pairs and the grand-canonical ensemble contains single-particle or hole excitations which have come from the reservoir that causes the essential difference between the two ensembles.

As will be shown in the section on the grand-canonical ensemble below, the contributions to the partition function due to up to five additional holes or electrons from the ground state with N particles give a sizable fraction of the coefficient of $\pi^2/3$ which is characteristic of the degenerate free-electron gas.

III. CANONICAL PARTITION FUNCTION

In this section we will outline the evaluation of the canonical partition function using the cumulant-summation formula written out above. The first step is to begin with the standard formula for the partition function for N free electrons with single-particle energies $\epsilon_{\mathbf{k}s}$ for momentum $\mathbf{k}$ and spin s,

$$Q_N = \frac{1}{N!}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_N}{}' \exp\left(-\beta\sum_{i=1}^{N}\epsilon_{\mathbf{k}_i s_i}\right), \tag{3.1}$$

where the prime on the sum indicates that terms where any two particles have the same momentum and spin are excluded from the sum. To simplify the counting factors we have included the prefactor of $N!$. Such an overall factor cannot change the thermodynamics. In order to simplify the writing of the equations the spin variables have been left off the summation variables in Eq. (3.1), but the reader should consider them to be included in the summation implicitly. Below, the presence of the spin variables will be explicitly indicated, where needed. At this stage the prime on the summation symbol is the only manifestation of the Pauli exclusion principle beyond the fact that the ground state is constructed using it.

Since we are interested in the low-temperature properties of the free-electron-gas partition function, we start with a ground state which is the filled Fermi sea: all states with momentum below the Fermi momentum $|\mathbf{k}_F|$ are occupied and all states with larger momentum are unoccupied. For later simplicity of notation we designate the set of occupied momenta by the set $\mathcal{F}$.

In the following paragraphs we set a convention that momentum variables representing states not in the Fermi sea will be represented by $\mathbf{p}$ and momentum variables representing states inside the Fermi sea will be represented by $\mathbf{q}$.

We rearrange the terms in Eq. (3.1) so they are collected together by the number of particle-hole excitations out of the Fermi sea. We label each set of terms by $t_n/n!$, where n is the number of particle-hole excitations. In such a rearrangement the first term corresponds to no particles excited out of the Fermi sea and can be written as

$$t_0 = \frac{1}{N!} \sum_{q_1,\ldots,q_N}{}' \exp\left(-\beta \sum_{i=1}^{N} \epsilon_{\mathbf{q}_i s}\right) . \tag{3.2}$$

There are exactly $N!$ ways the q_i can be assigned the N specific values contained in $\mathcal{F}$. For each of these $N!$ assignments the argument of the exponential is E_0, and the value of t_0 becomes

$$t_0 = e^{-\beta E_0}. \tag{3.3}$$

The single-particle–hole pair excitations contribute the term t_1 which will have a sum over $N-1$ q's and one p,

$$t_1 = \frac{1}{N!} \sum_{q_1,\ldots,q_{N-1},p}{}' \exp\left(-\beta \sum_{i=1}^{N-1} \epsilon_{\mathbf{q}_i s}\right) \exp(-\beta \epsilon_{\mathbf{p}s}). \tag{3.4}$$

Each term in this series can be represented much more simply by noting that it represents a single hole in the Fermi sea. Therefore the argument of the first exponential in Eq. (3.4) can be written as

$$\sum_{i=1}^{N-1} \epsilon_{\mathbf{q}_i s} = E_0 - \epsilon_q . \tag{3.5}$$

Remember that there are $N!$ ways to distribute N electrons in a system with certain momentum configuration, so we have

$$t_1 = \sum_{\mathbf{p},s,\mathbf{q},s'}{}' e^{-\beta E_0} \exp(-\beta \epsilon_{\mathbf{p}s}) \exp(+\beta \epsilon_{\mathbf{q}s'}). \tag{3.6}$$

For later purposes it is useful to introduce a diagrammatic representation for the sums in Eq. (3.6). We represent the momentum (and spin) sums over the initially unoccupied particle states by (•) and the sum over hole momenta (and spins) by (∘). Since the particle and hole sums are independent we will be able to write t_1 as either

$$t_1 e^{\beta E_0} = (\bullet\circ) = (\bullet)(\circ), \tag{3.7}$$

where we have factored out both the common exponential factor between t_0 and t_1.

The two particle-hole contributions to the partition function can be derived in much the same fashion as above. This begins by recognizing that each $N-2$ particle Fermi sea is best represented by the two holes q_1 and q_2, and that if the pair of holes is interchanged, the system remains the same. Therefore it is necessary to divide the summation over all possible q_1 and q_2 by 2! in order to avoid overcounting. This same factor also exists for sums over p_1 and p_2. These arguments lead to

$$t_2 = \frac{1}{2!} \sum_{q_1,q_2,p_1,p_2}{}' e^{-\beta\Delta_1} e^{-\beta\Delta_2} e^{-\beta E_0}, \tag{3.8}$$

where $\Delta_i = \epsilon_{p_i} - \epsilon_{q_i}$ and the prime on the sum implies the Pauli exclusion principle where no two particles (or holes) can have the same momentum and spin. Using the diagrammatic notation we can write the following for t_2:

$$\begin{aligned} 2!t_2 e^{\beta E_0} &= \sum_{q_1,q_2,p_1,p_2}{}' e^{-\beta\Delta_1} e^{-\beta\Delta_2} \\ &= (\bullet\circ\bullet\circ)'. \end{aligned} \tag{3.9}$$

Since the holes and particles do not have the same range of momenta, we may neglect the Pauli exclusion principle between them and write

$$(\bullet\circ\bullet\circ)' = (\bullet\bullet)'(\circ\circ)' . \tag{3.10}$$

By a similar argument it can be shown that the general term can be written as

$$t_n n! e^{\beta E_0} = \sum_{q_1,\ldots,q_n,p_1,\ldots,p_n}{}' \exp\left(-\beta \sum_{i=1}^{n} \Delta_i\right), \tag{3.11}$$

or symbolically

$$t_n n! e^{\beta E_0} = (\bullet\circ\cdots\bullet\circ)', \tag{3.12}$$

where the number of (•∘) pairs in the parentheses is n.

Using this symbolic notation we find that the canonical partition function for N free electrons can be written as

$$\begin{aligned} Q_N e^{\beta E_0} = {} & 1 + (\bullet\circ) + \frac{1}{2!}\frac{(\bullet\circ\bullet\circ)'}{2!} + \frac{1}{3!}\frac{(\bullet\circ\bullet\circ\bullet\circ)'}{3!} \\ & + \cdots + \frac{1}{n!}\frac{(\bullet\circ\cdots\bullet\circ)'}{n!} + \cdots , \end{aligned} \tag{3.13}$$

where the last term has n (•∘) pairs.

This is the series that we will attempt to sum using the cumulant-summation formula from which we seek a formula for Q_N of the form

$$Q_N = e^{-\beta E_0} \exp[\Theta(T,N)]. \tag{3.14}$$

Now each of the terms has a prime indicating that the summations must be carried out with the Pauli exclusion in effect. The cumulants will enable the systematic treatment of the Pauli exclusion. However, it is instructive and heuristically useful first to derive an approximation that will give the dominant low-temperature approximation. This approximation is simply to consider Θ to be equal to the first cumulant κ_1,

$$\Theta = \kappa_1 = (\bullet\circ). \tag{3.15}$$

Another way to think about this approximation is to neglect the primes on the diagrams in Eq. (3.13) and to factor each diagram into independent pairs of $(\bullet\circ)$. Equivalently, keeping only the first cumulant ignores the Pauli exclusion principle except insofar as it was used to construct the Fermi sea.

The evaluation of $(\bullet\circ)$ is very easy:

$$(\bullet\circ) = \sum_{\mathbf{p},s} \exp(-\beta\epsilon_{\mathbf{p},s}) \sum_{\mathbf{q},s} \exp(\beta\epsilon_{\mathbf{q},s}). \tag{3.16}$$

If we assume a constant density of states per electron of 2ρ and a band from $-D$ to D, we can write the sums as simple integrals

$$(\bullet\circ) = N^2(2\rho)^2 \int_0^D e^{-\beta\epsilon} d\epsilon \int_{-D}^0 e^{\beta\epsilon} d\epsilon, \tag{3.17}$$

so that at low temperatures we have that

$$(\bullet\circ) = \left(\frac{2\rho N}{\beta}\right)^2. \tag{3.18}$$

Inserting Eq. (3.18) into the heuristic approximation for Q_N gives a heat capacity of

$$C = 12N^2\rho^2 k_B^3 T^2, \tag{3.19}$$

where k_B is the Boltzmann constant.

The fact that the simplest approximation for Q_N does not yield an extensive exponential power, and does not recover the expected linear T heat capacity, is not due to our neglect of the Pauli exlcusion principle in this approximation. The contributions from the higher cumulants do not include linear particle number and temperature dependences. The Pauli exclusion principle can be taken into account exactly as will be illustrated in the following paragraphs and the Appendix. The canonical ensemble with its severely restricted excitations cannot exhibit the extensive and linear heat capacity for this system. In our discussion of the grand-canonical partition function below, we shall see that the fluctuations in the particle number are critical for recovering the extensitivity and the linear heat capacity.

Before examining the grand-canonical ensemble, let us discuss the first few corrections to this simple result for the canonical partition function and demonstrate the manner in which the Pauli exclusion principle can be included. This requires that we discuss the next few terms and cumulants in the series.

The second-order term in the sum t_2 is given by

$$t_2 = \frac{1}{2!}(\bullet\bullet)'(\circ\circ)'. \tag{3.20}$$

In the Appendix it is shown that the Pauli exclusion principle summation restrictions in the sum represented by $(\bullet\bullet)'$ can be carried out by adding in and subtracting out the excluded terms. Using these results from the Appendix we see that

$$t_2 = \tfrac{1}{2}(16x^4 - 8x^3 + x^2), \tag{3.21}$$

where $x = N\rho/\beta$. Combining this with $t_1 = 4x^2/N$, we can calculate the second cumulant

$$\kappa_2 = -8x^4 - 4x^3 + \tfrac{1}{2}x^2. \tag{3.22}$$

Now the first few terms of the exponential argument can be written as

$$\Theta = \tfrac{17}{4}x^2 - 2x^3 - 4x^4, \tag{3.23}$$

where Θ is clearly not extensive.

Higher-order corrections can be carried out for the canonical ensemble, but will not be completed here. The higher-order terms represent higher powers of the particle number N and the temperature T and do not change the basic result that the canonical ensemble does not give the expected temperature dependence and extensivity. The fact that Θ from this cumulant expansion calculation is not extensive is rather surprising. Since the Θ series appears to converge only for small values of x, our result may only reflect the series expansion of an analytical function in the small x regime, whereas the same function should be extensive at the large x (i.e., large N) limit. The simplest class of such analytical functions can be obtained by factoring x^2 out of the Θ series and seeking the $[M, M-1](x)$ Padé approximant[12] for the remaining series:

$$\Theta = x^2[M, M-1](x), \tag{3.24}$$

where $[M, M-1](x)$ is defined as

$$[M, M-1](x) = \frac{\alpha_0 + \alpha_1 x + \cdots + \alpha_{M-1}x^{M-1}}{\beta_0 + \beta_1 x + \cdots + \beta_M x^M} \tag{3.25}$$

in which α's and β's are constants to be determined from the expansion of Θ in the small x regime. In the large x limit, the leading term of Θ from Eq. (3.24) is proportional to x, thus proportional to the particle number N. Evaluation of the leading coefficients for large x was carried out with several terms and the corresponding Padé approximants. There was no convergence as the order of the Padé approximants and partial sums increased, and the values of the heat capacity did not correspond to the grand-canonical ensemble result. In any case, we have demonstrated that the "proof" of the equivalence between the canonical and grand-canonical ensembles is not as trivial as indicated in standard textbooks. The rest of the paper will focus on the experimentally more important grand-canonical ensemble.

IV. THE GRAND PARTITION FUNCTION

The formula for the grand partition function is a sum of terms $\exp\{\beta[N'\mu - E'_N(\alpha)]\}$ for all possible numbers of particle numbers N' and all states α for each N'. When we want to compare with the evaluation for a system of N particles, we can rewrite the series by first summing all of the terms for N particles, then summing all of the states for $N+1$ particles, $N-1$ particles, $N \pm 2$, etc. Symbolically, we can write the grand partition function as

$$\begin{aligned}\mathcal{Z}\exp[-\beta(N\mu - E_0)] = {} & \cdots + (\circ\circ)'/2! + (\circ\,\circ\,\bullet\circ)'/3! + \cdots \\ & +(\circ) + (\circ\bullet\circ)'/2! + \cdots 1 + (\bullet\circ) + (\bullet\circ\bullet\circ)'/(2!)^2 + \cdots + (\bullet) + (\bullet\bullet\circ)'/2! + \cdots \\ & +(\bullet\bullet)'/2! + (\bullet\,\bullet\,\bullet\circ)'/3! + \cdots + \cdots \,. \qquad (4.1)\end{aligned}$$

Here the terms in the partition function are written in lines by the particle number in the system. The first line displayed is for $N-2$, the next lines are for $N-1$, N, $N+1$, $N+2$, etc. The line including the 1 represents the terms included in the canonical ensemble for N particles.

For the purpose of applying the cumulant formula we need to regroup the terms by dominant powers of the number of particles. (That is, we group all terms that go as N together, all N^2 terms together, etc.) If we carry this out, we can write the partition function as

$$\begin{aligned}\mathcal{Z}\exp[-\beta(N\mu - E_0)] = {} & 1 + (\bullet) + (\circ) + \frac{1}{2!}[(\bullet\bullet)' + (\circ\circ)' + 2(\bullet\circ)] + \frac{1}{3!}[(\bullet\bullet\bullet)' + (\circ\circ\circ)' + 3(\bullet\circ\circ)' + 3(\circ\bullet\bullet)'] \\ & + \frac{1}{4!}[(\bullet\,\bullet\,\bullet\bullet)' + (\circ\,\circ\,\circ\circ)' + 4(\bullet\,\circ\,\circ\circ)' + 4(\circ\,\bullet\,\bullet\bullet)' + 6(\bullet\,\bullet\,\circ\circ)'] + \cdots \,. \qquad (4.2)\end{aligned}$$

Note that only the 1 and the terms with equal numbers of particles and holes represent the contributions from the canonical ensemble. In Eq. (4.2) there are only two such terms explicitly shown excluding the initial 1. Most of the terms displayed in Eq. (4.2) represent small fluctuations in particle number. To evaluate $\mathcal{Z}$ using the cumulant formula we need to calculate the various cumulants. Using the results from the Appendix we have the following:

$$\kappa_1 = t_1 = (\bullet) + (\circ) = 4x, \qquad (4.3)$$

where $x = N\rho/\beta$. It should be noted that it is κ_1 that determines the major temperature dependence of the partition function. In this case the contributions to κ_1 represent fluctuations in the particle number by ± 1. The first contribution from the N particle states arises not in t_1 but in t_2. To evaluate t_2 it is necessary to evaluate

$$t_2 = (\bullet\bullet)' + (\circ\circ)' + 2(\bullet\circ). \qquad (4.4)$$

Using the results of the Appendix it is easy to show that $t_2 = 16x^2 - 2x$. Note that, since x is proportional to the number of particles, t_2 is of order N^2. When we calculate the second cumulant, it is found to be extensive as required:

$$\kappa_2 = t_2 - t_1^2 = -2x. \qquad (4.5)$$

Combining these two results to determine the first approximation to Θ we find the first two terms in the series for $\pi^2/12$,

$$\Theta = 4x(1 - 1/2^2). \qquad (4.6)$$

The next two terms in the series t_3 and t_4 can be picked out of Eq. (4.2). Using the results of the Appendix it is easy to show that

$$t_3 = 64x^3 - 24x^2 + \tfrac{8}{3}x, \qquad (4.7)$$

$$\kappa_3 = \tfrac{8}{3}x, \qquad (4.8)$$

$$t_4 = 256x^4 - 192x^3 + (\tfrac{128}{3} + 12)x^2 - 6x, \qquad (4.9)$$

$$\kappa_4 = -6x. \qquad (4.10)$$

The higher-order terms begin to be significantly more complicated. We have evaluated t_5 and κ_5 using the computer-based algebra manipulation program MATHEMATICA.[13] The combination of all of the cumulants evaluated including t_5 yields

$$\Theta = 4x\left(1 - \frac{1}{2^2} + \frac{1}{3^2} - \frac{1}{4^2} + \frac{1}{5^2}\right) \qquad (4.11)$$

which is within 1.96% of the correct coefficient.

V. CONCLUSIONS

This research originated in an attempt to explore methods for many-body calculations which dealt directly with the many-particle states and did not start with the independent single-particle approximation. The fact that the grand-canonical partition function can be approximated in this way indicates that this approach may have merit for more complex interacting systems. Indeed, calculations using this approach have been started.

The result that there is a difference between the canonical and grand-canonical ensembles has been quite surprising. Since the difference seems to be to arise from the distinctly different terms that are allowed in the sums of the two ensembles, there seems to be no way to avoid the results of this study. This descrepancy raises a number of questions that merit further study.

The first question arises from the surprisingly strong role that extremely small fluctuations in particle number play in the low-temperature properties of the free-electron gas. Our traditional understanding has assumed that experimental measurements should be most closely described by the canonical ensemble for a fixed number of particles. Indeed, all comparisons of calculated heat capacities use the formula for $C_{(N)}$ derived from the grand-canonical ensemble in which the chemical potential changes with temperature to constrain the average number of particles to be equal to N.

The fact that the canonical ensemble does not have an extensive exponential argument, and does not agree qualitatively with experiment, suggests that heat-capacity experiments might be compared instead with C_μ, where μ at $T = 0$ is determined by the particle number. Using C_μ instead of $C_{\langle N \rangle}$ for a free-electron-gas density of states would give rise to an increase in the theoretical estimate by a factor of 1.5. A cursory comparison of reported experimental heat capacities[14] and band theory calculations for simple metals[15] shows that for Li and other few-electron systems the ratio of experimental to theoretical $C_{\langle N \rangle}$ is greater than 1 and close to 1.5. For more complicated systems there is no correlation with this simple picture. Since no consideration has been made here of corrections due to the Coulomb interaction, the lack of agreement is not unexpected.

Nevertheless, the role that particle-number fluctuation plays in the thermodynamics of the free-electron gas raises the question of validity for approximation schemes where it is implicitly assumed that the canonical ensemble most closely represents experimental measurements. These questions should be studied for other systems.

The application of these ideas to an interacting system, such as a Hubbard Hamiltonian, appears to be tractable, at least to the inclusion of the first few κ_n. The procedure would select a basis set of many-particle states $|\psi\rangle$ which may be close to eigenvectors of the Hamiltonian. Approximations will be constructed for the resolvents of the Hamiltonian H with these states and terms t_n will be evaluated by using contour integrals of the type

$$\int dz \langle\psi|(z-H)^{-1}|\psi\rangle e^{-\beta z}. \tag{5.1}$$

By collecting terms representing the same number of excitations above, an approximate ground state in much the same way as in Eq. (4.2), it is possible to approximate the first few cumulants κ_n. This study will be described elsewhere.

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APPENDIX

In this appendix the details of the energy sums will be briefly listed.

The sum of the exponential of the excited electron states is given by

$$(\bullet) = \sum_{\mathbf{p},s} \exp[-\beta(\epsilon_{\mathbf{p}s} - \mu)]. \tag{A1}$$

For simplicity in this paper we will assume that the density of states per spin and per particle for the electrons is constant over a bandwidth of $2D$ with value ρ. At low temperatures the sum in Eq. (A1) is $(\bullet) = 2x$, where

$$x = N\rho/\beta, \tag{A2}$$

and we have neglected exponentially small terms. The sum over the hole states yields the same result:

$$(\circ) = \sum_{\mathbf{q},s} e^{\beta(\epsilon_{\mathbf{q}s}-\mu)}. \tag{A3}$$

or that $(\circ) = 2x$.

The first example of the effect of the Pauli exclusion principle arises in the two-particle (two-hole) sums. The two-particle sum $(\bullet\bullet)'$ contains both momentum and spins sums and the restriction is that no two electrons can be in the same state $(\mathbf{p}, s)$,

$$(\bullet\bullet)' = \sum_{\mathbf{p}_1,s_1,\mathbf{p}_2,s_2}{}' e^{-\beta(\epsilon_{\mathbf{p}_1 s_1}-\mu)} e^{-\beta(\epsilon_{\mathbf{p}_2 s_2}-\mu)}. \tag{A4}$$

If $s_1 \neq s_2$, then the momentum sums are unrestricted and the evaluation reduces to $4x^2$. If the two spins are equal, then the prime in the summation reminds us that the two momenta cannot be equal. For later use it is helpful to define the sums without the spins using square brackets:

$$[\bullet\bullet]' = \sum_{\mathbf{p}_1,\mathbf{p}_2}{}' e^{-\beta(\epsilon_{\mathbf{p}_1}-\mu)} e^{-\beta(\epsilon_{\mathbf{p}_2}-\mu)}. \tag{A5}$$

The summation restriction can be eliminated by adding and subtracting out the terms with both momenta equal and having no restriction on the momentum sums. This is most easily written with a δ function:

$$[\bullet\bullet]' = \sum_{\mathbf{p}_1,\mathbf{p}_2} e^{-\beta(\epsilon_{\mathbf{p}_1}-\mu)} e^{-\beta(\epsilon_{\mathbf{p}_2}-\mu)} (1 - \delta_{\mathbf{p}_1,\mathbf{p}_2}). \tag{A6}$$

In this equation there are no restrictions on the sums and we may write this equation symbolically as

$$[\bullet\bullet]' = [\bullet]^2 - [\bullet - \bullet], \tag{A7}$$

where the second term represents a single momentum sum of all terms with both momenta equal. It is straightforward to show that $[\bullet] = x$ and that

$$[\bullet - \bullet] = x/2. \tag{A8}$$

With these rules we can evaluate Eq. (A4), taking into account the factor of 2 for the spin values:

$$(\bullet\bullet)' = 2[\bullet\bullet]' + 2[\bullet\bullet], \tag{A9}$$

$$(\bullet\bullet)' = 2([\bullet]^2 - [\bullet - \bullet]) + 2[\bullet]^2. \tag{A10}$$

So we have that $(\bullet\bullet)' = 4x^2 - x$, which is the same value as for $(\circ\circ)'$.

For the evaluation of the grand-canonical ensemble it is necessary to evaluate more complicated diagrams. The first one of these is $(\bullet\ \bullet\ \bullet)'$, which will involve three spin sums and three momentum sums. If we consider the eight different spin terms, we find that there are two with all spins the same and six with two spins the same. This means that we can write this three-particle term in terms of the square brackets which contain only momentum sums. That is,

$$(\bullet\bullet\bullet)' = 2[\bullet\bullet\bullet]' + 6[\bullet][\bullet\bullet]'. \tag{A11}$$

The momentum restrictions in the three-electron bracket can be removed by three δ-function factors multiplying the momentum sums,

$$(1-\delta_{p1,p2})(1-\delta_{p2,p3})(1-\delta_{p1,p3}). \tag{A12}$$

Working out the sums and the δ functions yields

$$[\bullet\bullet\bullet]' = [\bullet]^3 - 3[\bullet][\bullet-\bullet] + 2[\bullet-\bullet-\bullet]. \tag{A13}$$

From this result and using Eq. (A9), it can be shown that

$$(\bullet\bullet\bullet)' = 8x^3 - 6x^2 + \frac{4x}{3}. \tag{A14}$$

We also have, as before, that $(\bullet\bullet\bullet)' = (\circ\circ\circ)'$.

The four-particle sum can be worked out in a similar fashion. The four-spin sums give two terms with all spins equal, eight terms with three spins the same, and six terms with two spins the same. This leads to the following equation:

$$(\bullet\bullet\bullet\bullet)' = 2[\bullet\bullet\bullet\bullet]' + 8[\bullet][\bullet\bullet\bullet]' + 6[\bullet\bullet]'[\bullet\bullet]'. \tag{A15}$$

The Pauli exclusion summation restrictions can be lifted by including δ-function factors and a lengthy graphical analysis leads to the following:

$$\begin{aligned}[\bullet\bullet\bullet\bullet]' = {} & [\bullet]^4 - 6[\bullet]^2[\bullet-\bullet] + 8[\bullet][\bullet-\bullet-\bullet] \\ & +3[\bullet-\bullet]^2 - 6[\bullet-\bullet-\bullet-\bullet]. \end{aligned} \tag{A16}$$

Substitutions from the above yield

$$(\bullet\bullet\bullet\bullet)' = 16x^4 - 24x^3 + \tfrac{41}{3}x^2 - 6x. \tag{A17}$$

Higher-order contributions can be worked out with relative ease using something like MATHEMATICA. We have worked out the fifth-order diagrams in this way.

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