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Ursell operators in statistical physics I: Generalizing the Beth Uhlenbeck formula

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Abstract. — The Beth Uhlenbeck formula gives an exact (quantum) expression of the second virial correction to the equation of state of a (slightly degenerate) dilute gas. We show how this result can be extended to arbitrary degeneracy provided that the interaction potential has a sufficiently short range. For this purpose we develop a formalism based on the use of Ursell operators, which contain no symmetrization in themselves (they correspond to an auxiliary system of distinguishable particles) and we show how they can also be used for a system of identical particles. A concise expression generalizing the Beth Uhlenbeck formula is obtained, which is equally valid for bosons and fermions. Higher order corrections are also introduced. The formalism is rather general and will be applied to other cases in forthcoming articles.

1. Introduction

The Beth Uhlenbeck formula [1, 2] gives an exact expression of the second virial coefficient as a function of all collision phase shifts associated with the interaction potential. This is a remarkable result which, in a concise formula including no phenomenological constant, relates macroscopic and microscopic quantities: on the one hand, the density, the temperature, and the pressure of a gas, on the other hand, the quantum phase shifts, which are exactly calculable from the Schrödinger equation. A closer inspection shows that the pressure correction is the sum of two contributions, one of pure statistics, and a second arising from the interactions; the former is actually nothing but the first-order term of the expansion in $n\lambda^3$ of the ideal gas equation of state (n is the number density and λ the thermal wavelength). It is therefore not surprising that the validity of the formula should require two conditions, that the gas be dilute with respect to both degeneracy effects ($n\lambda^3 \ll 1$) and interaction effects as well ($nb^3 \ll 1$, where b is the range of the interaction potential). A natural question is whether one can release the first of these conditions and study gaseous systems over a larger range, going continuously from the classical region where $n\lambda^3 \ll 1$ to the quantum region where this quantity is comparable to one. One would just assume that the gas remains always dilute in terms of the interactions. As a matter of fact, most classical textbooks on quantum statistical mechanics include a study of gaseous systems that are degenerate and imperfect. The methods

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they use are based on various forms of perturbation theory; for instance they introduce an auxiliary pseudopotential which replaces the real interaction potential [3], or they make a direct substitution of a collision T matrix for this potential [4], or use variational methods [5]. This well known approach is, nevertheless, different from that of Beth and Uhlenbeck whose calculation is exact (of course they limit the calculation to the first density correction to the equation of state, but this is precisely the definition of the second virial correction). In essence, the cluster expansion method they use is a method providing directly density expansions, as opposed to interaction expansions, which require at least partial resummations of diagrams in powers of the interaction potential [6] to reconstruct the T matrix from V and to obtain density expansions. Actually, the exact treatment of the relative motion of two particles is explicit in the Beth Uhlenbeck formula, which contains a thermal exponential of the two particle Hamiltonian ensuring that thermal equilibrium has been reached, in other words that the binary correlations between the particles are treated properly. Technically, a characteristic of this approach is that no expression which diverges for repulsive hard cores is ever written, even at some intermediate stage. It therefore seems to be an attractive possibility to try and extend the method to degenerate systems, if only to compare the result of both methods, interaction and density expansions. This is the subject of the present article; we show that concise and exact formulas can indeed be written that provide a natural generalization of the Beth Uhlenbeck formula, without requiring complicated algebra.

For this purpose, we will make use of a generalization of the quantum Ursell ⁽¹⁾ cluster functions introduced initially by Kahn and Uhlenbeck [7]: Ursell operators which intrinsically do not contain statistics (as opposed to the usual quantum Ursell functions [9, 10], which are fully symmetrized). The action of the operators is defined, not only in the space of symmetric or antisymmetric states of the real system, but also in the larger space of an auxiliary system of distinguishable particles. If the system is dilute in terms of the interactions but not of statistics, this makes it possible to limit the calculation to low order Ursell operators while, with the usual (fully symmetrized) Ursell functions, one would need to include higher and higher orders with increasing degeneracy ⁽²⁾. Of course, this method implies that we have to give up well-known advantages of the formalism of second quantization, but this is the price to pay for the treatment of interactions and statistics in completely independent steps. It also means that an explicit symmetrization of the wave functions becomes indispensable at some point and, moreover, that no approximation whatsoever can be made at this step: otherwise the possibility of treating strongly degenerate systems would be lost. Fortunately it turns out that the symmetrization operation can indeed be performed exactly. This is done by introducing simple products of operators, corresponding to exchange cycles, or more generally simple functions of operators (fractions) that correspond to summations over the size of these cycles up to infinity. Physically, this allows us to emphasize the role of the size of exchange cycles [11] that take place in a physical system of identical particles and shows, in each situation, which size is dominant in the determination of its properties, pressure for instance.

Another feature of the method is that it naturally provides expressions for the one- and two-body density operators, which is of course convenient if one is interested in a detailed study of correlations. Also, the formalism can be applied to other physical problems, such as the Bose-Einstein condensation. These questions will be the subject of coming articles; a preliminary report on this work has been given in [11].

⁽¹⁾ The initial introduction of the Ursell functions was made by him within classical statistical mechanics [8], and generalized ten years later to quantum mechanics by Kahn and Uhlenbeck.

⁽²⁾ As discussed in [11], when a Bose Einstein condensation takes place, the Ursell operators have no singular variation, which is another way to see that they are not sensitive to degeneracy by themselves.

2. Ursell Operators

In the canonical ensemble, the partition function Z_N of a system of indistinguishable particles is given by a trace inside the space of symmetrical (or antisymmetrical) states. Nevertheless, with the help of the projectors S and A onto these (sub)spaces, the trace can be extended to a larger space, which is associated with the same number of distinguishable particles:

$$Z_N = \text{Tr} \left\{ K_N \begin{matrix} S \\ A \end{matrix} \right\} \tag{1}$$

In this equation, S applies for bosons while A applies for fermions, and the operators K_N are defined by:

$$\begin{aligned} K_1 &= \exp -\beta H_0(1) \\ K_2 &= \exp -\beta [H_0(1) + H_0(2) + V_{12}] \\ &\dots \\ K_N &= \exp -\beta \left[\sum_{i=1}^N H_0(i) + \sum_{i>j} V_{i,j} \right] \end{aligned} \tag{2}$$

with the usual notation: $H_0(1)$ is the one-particle Hamiltonian including kinetic energy and an external potential (if there is any in the problem), $V_{i,j}$ is the interaction potential between particles with labels i and j . We now use cluster techniques to expand operators exactly in the same way as one usually does for functions. The Ursell operators U_l ($l = 1, 2, \dots, N$) are therefore defined according to:

$$\begin{aligned} U_1 &= K_1 \\ U_2(1, 2) &= K_2(1, 2) - K_1(1)K_1(2) \\ U_3(1, 2, 3) &= K_3(1, 2, 3) - K_2(1, 2)K_1(3) - K_2(2, 3)K_1(1) \\ &\quad - K_2(3, 1)K_1(2) + 2K_1(1)K_2(2)K_1(3) \end{aligned} \tag{3}$$

etc.. Conversely, in terms of the Ursell operators, the N particle operator K_N can be written in the form:

$$K_N = \sum_{\{m'_i\}} \sum_{\{D'\}} \underbrace{U_1(\cdot)U_1(\cdot)\dots U_1(\cdot)}_{m'_1 \text{ factors}} \times \underbrace{U_2(\cdot, \cdot)U_2(\cdot, \cdot)\dots U_2(\cdot, \cdot)}_{m'_2 \text{ factors}} \times U_3(\cdot, \cdot, \cdot) \dots \tag{4}$$

where the first summation is made on all possible ways to decompose the number of particles as:

$$N = \sum_l l m'_l \tag{5}$$

The second summation corresponds to all non-equivalent ⁽³⁾ ways to distribute the N particles into the variables of the Ursell operators, symbolized by dots in (4). It is convenient to simplify

⁽³⁾ For instance $U_2(1, 2)U_3(3, 4, 5)$ and $U_2(2, 1)U_3(4, 3, 5)$ correspond to equivalent distributions of 5 particles, since the very definition of the Ursell operators implies that the order inside each U_l is irrelevant.

the two summations into one:

$$\sum_{\{m_i\}} \sum_{\{D'\}} \Rightarrow \sum_{\{U\}} \tag{6}$$

which is meant over all non-equivalent ways to distribute the particles into various sequences of U 's. There is little difference between our definitions and those of Section 4.2 of [9] or [10]: we use operators instead of symmetrized functions and, more importantly, the action of these operators is defined, not only within the state space that is appropriate for bosons or fermions, but also in the larger space obtained by the tensor product that occurs for distinguishable particles. Hence the need for an explicit inclusion of S or A in (1).

We now decompose these operators into a sum of permutations P_α that, in turn, we decompose into independent cycles C of particles (4):

$$\frac{S}{A} = \frac{1}{N!} \sum_{\{m_i\}} \sum_{\{D\}} \underbrace{C_1(\cdot)C_1(\cdot)C_1(\cdot)}_{m_1 \text{ factors}} \times \eta^{m_2} \underbrace{C_2(\cdot, \cdot)C_2(\cdot, \cdot)C_2(\cdot, \cdot)}_{m_2 \text{ factors}} \times C_3(\cdot, \cdot, \cdot) \dots \tag{7}$$

where the first summation is similar to that of (4), while the second corresponds to all non-equivalent (5) ways to distribute numbers ranging from one to N into the variables of the various C 's. In this equation, the operator S applies for bosons with $\eta = +1$, while A with $\eta = -1$ applies for fermions. We also simplify the notation into:

$$\sum_{\{m_i\}} \sum_{\{D\}} \Rightarrow \sum_{\{P_\alpha\}} \tag{8}$$

We can now insert (4) and (7) into (1) and obtain, within a double summation, numbers that are traces calculated in the space of distinguishable particles, i.e. in the ordinary tensor product of N single particle state spaces. Inside most of the terms of the summation, a factorization into traces taken inside smaller subspaces occurs. For instance, if the term in question contains a particle number i contained at the same time in a U_1 operator as well as in a C_1 , the contribution of that particle completely separates by introducing the simple number $\text{Tr}\{U_1\}$. Or, if n particles are all in the same U_n but all in separate C_1 's, this group of particles contributes by a factor $\text{Tr}_{1\dots n}\{U_n\}$; if they are all in different U_1 's but also contained in one single large cycle C_n , their contribution also factorizes separately. More generally, in each term of the double summation, particles group into clusters (U - C clusters), which associate together all particles that are linked either (6) by cycles C_l (with $l > 1$) or by Ursell operators $U_{l'}$ (with $l' > 1$). The general term is therefore the product of the contributions of all the clusters that it contains and one can write:

$$Z_N = \frac{1}{N!} \sum_{\{P_\alpha\}} \sum_{\{U\}} \prod_{\text{clusters}} \Gamma_{\text{cluster}}(i, j, k, \dots) \tag{9}$$

(4) We use the same notation as in reference [11]: $C_k(i, j, k, \dots)$ denotes a cycle where particle i replaces particle j , particle j replaces particle k , etc. This should not be confused with the notation $P(i, j, k, \dots)$ for a general permutation (not necessarily a cycle) where particle i replaces particle 1, particle j particle 2, particle k particle 3, etc. Any P can be decomposed into a product of C 's; for instance, $P(2, 1, 3) = C_2(1, 2)C_1(3)$.

(5) Inside every cycle, a circular permutation of the variables has no effect and therefore does not affect the permutation P_α .

(6) There are therefore two explicitly distinct origins to the clustering of particles in this point of view: belonging to the same $U_{l'}$ or to the same cycle C_l . This is distinct from usual cluster theories where, either only interactions introduce clustering (as in classical statistical mechanics), or the two origins are not explicitly distinguished (as in usual quantum cluster theory).

where (i, j, k, \dots) is the index number of particles contained within the cluster; the number of clusters into which each term of the double summation is factorized depends, in general, on this particular term.

3. Diagrams

Clusters differing only by the numbering of particles that they contain give the same contribution. It is therefore useful to reason in terms of diagrams ($U-C$ diagrams), which emphasize the way particles are connected through exchange cycles and Ursell operators, rather than their numbering. For instance, the first diagram will correspond to one particle in a U_1 and in a C_1 (whatever the numbering of the particle is), and contribute the value $\text{Tr} \{U_1\}$ as mentioned above; another diagram will introduce the value $\text{Tr}_{1,2} \{U_2\}$, etc.; in this section we discuss more generally how diagrams can be defined in a convenient way.

3.1. DEFINITION AND COUNTING. — The value of any diagram containing n_{diag} particles can be written as a trace over the variables of n_{diag} particles numbered arbitrarily:

$$\Gamma_{\text{diag.}} = \eta^{p_2+p_4+\dots} \text{Tr}_{1,2,\dots,n_{\text{diag}}} \{U_1(1)..U_1(r_1)U_2(r_1+1, r_1+2)..C_1(i). C_1(j)C_2(l, s). \dots\} \quad (10)$$

Here p_k is the number of cycles ⁽⁷⁾ of length k ; the factor $\eta^{p_2+p_4+\dots}$ arises from the factors η 's in (7) and corresponds to the contribution of the parity of the permutations contained in the diagram to the total permutation of the N particles. Now, inside each term of the multiple summation, a given diagram $\Gamma_{\text{diag.}}$ may occur several times; we then note $m_{\text{diag.}}$ the number of times it is repeated, and we get:

$$Z_N = \frac{1}{N!} \sum_{\{P_\alpha\}} \sum_{\{U\}} \prod_{\text{diag.}} [\Gamma_{\text{diag.}}]^{m_{\text{diag.}}} \quad (11)$$

with the obvious relation:

$$N = \sum_{\text{diag.}} m_{\text{diag.}} \times n_{\text{diag.}} \quad (12)$$

Of course identical diagrams appear, not only in the same term of the double summation, but also in many different terms. Therefore, if $\sum_{\{m_{\text{diag.}}\}}$ symbolizes a summation over all possible ways to decompose N according to (12), we can also write:

$$Z_N = \frac{1}{N!} \sum_{\{m_{\text{diag.}}\}} c \{m_{\text{diag.}}\} \times \prod_{\text{diag.}} [\Gamma_{\text{diag.}}]^{m_{\text{diag.}}} \quad (13)$$

where $c \{m_{\text{diag.}}\}$ is the number of terms in the double summation of (11) that correspond to this particular decomposition of N .

To evaluate this number, we have to specify more precisely how the $U-C$ diagrams are constructed. In every cluster, we represent the permutation cycles C_k by horizontal lines containing k boxes, or segments, which are available to numbered particles. When the corresponding particles are inside U_1 's, we do not add anything to the diagram; when they are contained inside U_2 's, we join the corresponding segments by an additional double line, a triple line for U_3 's, etc. For instance, if we consider the pure exchange cluster:

$$\Gamma_{\text{cluster}} = \text{Tr}_{1,2,\dots,7} \{U_1(1)U_1(2)..U_1(7)C_7(1, 2, \dots, 7)\} \quad (14)$$

⁽⁷⁾ One obviously has: $p_1 + 2p_2 + \dots = n_{\text{diag}}$.

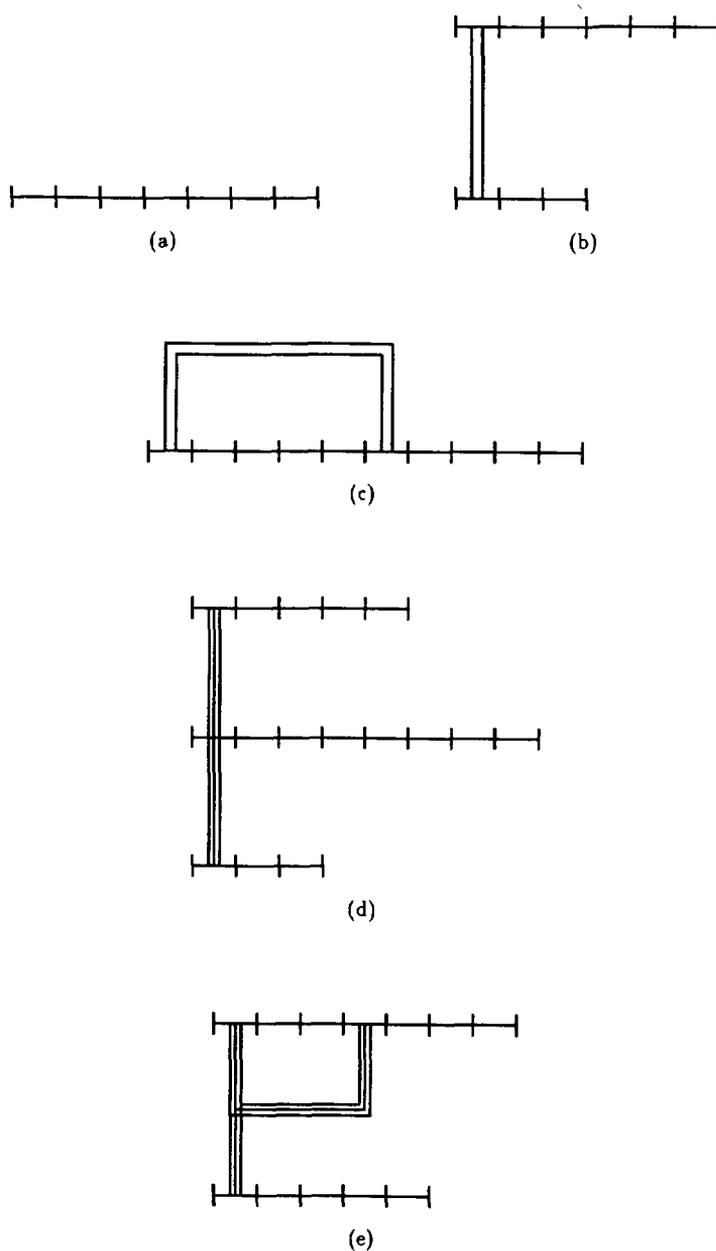


Fig. 1. — Examples of U - C diagrams. For an ideal gas, only linear U - C diagrams containing chains of one-particle Ursell operators U_1 occur, as shown in (a); a summation of the contribution of these diagrams over the length of the chain gives the grand potential (multiplied by $-\beta$). The generalization of the Beth Uhlenbeck formula arises from the diagrams shown in (b) and (c) containing one single two-body Ursell operator U_2 ; for each of them, a summation over the lengths of the U_1 chains is also necessary. Figure (d) shows an example of a diagram containing a three-body U_3 operator and three U_1 chains, with a counting factor $g = 2$. Figure (e) shows an example of multiple connection through an U_3 operator, which also introduces a factor $g = 2$ in the weight of the diagram. For more details on the definition and counting of the diagrams, see Appendix A.

the corresponding diagram will be that of Figure 1a. This kind of linear diagram is the only possibility for an ideal gas; to generate a Γ_{cluster} appearing in (9), it must receive a numbered particle in the first segment of the line, in the second the particle which is replaced by it under the effect of the permutation cycle, in the third the particle which is replaced by that in the second segment, etc. Equation (14) gives what we will call the "explicit value" of the contribution of the diagram; using simple transformations (see Ref. [11] or Sect. 4.1), one can obtain the simpler "reduced value" $\text{Tr}_1 \{ [U_1(1)]^7 \}$.

If we now start from a cluster which contains one single U_2 :

$$\Gamma_{\text{cluster}} = \text{Tr}_{1,2,\dots,9} \{ U_2(1,2)U_1(3)U_1(4)U_1(5)..U_1(9)C_3(1,3,4)C_6(2,5,\dots,9) \} \quad (15)$$

we obtain the diagram shown in Figures 1b; in the same way, the cluster:

$$\Gamma_{\text{cluster}} = \text{Tr}_{1,2,\dots,10} \{ U_2(1,6)U_1(2)U_1(3)..U_1(10)C_{10}(1,2,3,\dots,6,\dots,10) \} \quad (16)$$

leads to the diagram of Figure 1c. These two kinds of diagrams turn out to be the only ones that are necessary to generalize the Beth Uhlenbeck formula; we give their reduced values in Section 4.2. Figure 1d shows an example of a diagram containing one single U_3 , and arising from the trace:

$$\Gamma = \text{Tr}_{1,2,\dots,16} \{ U_3(1,2,3)U_1(4)U_1(5)..U_1(16)C_3(1,4,5)C_8(2,6..12)C_5(3,..16) \} \quad (17)$$

and Figure 1e gives another similar example. Clearly, the process can be generalized to associate a diagram to any cluster, however large and complex.

But it is not sufficient to construct diagrams, we must also choose explicit rules ⁽⁸⁾ ensuring that every Γ_{cluster} appearing in (9), where the particles are still numbered, will correspond to one single, well defined, diagram; for instance, for the cluster written in (15), we must decide whether the diagram will be that shown in Figure 1b or another where the lowest cycle ("base cycle") is that of length 6 instead of 3. We will avoid this kind of ambiguity by choosing rules which fix, for every cluster associated with a given diagram, where exactly each numbered particle should fall into the diagram. These rules ensure that no double counting of clusters may occur; they also determine how the geometrical characteristics of the diagrams (the lengths of the successive cycles) can be varied, which in turn determines the way in which the summations over lengths will be made in a second step (next section). For our purpose in this article, we do not need to study the most general case (this discussion is given in Appendix A); it will be sufficient to remember that the first particle in the lowest cycle ("base cycle") must be, among all particles contained in the U_l of highest order l , that which has the lowest index number for the configuration to be correct.

The preceding rules also introduce the "counting factors" corresponding to the probability of obtaining a correct representation of a cluster by throwing numbered particles at random into a diagram; the counting factors are used below to obtain the value of $c \{ m_{\text{diag.}} \}$. Suppose for instance that we distribute k numbered particles into a linear diagram of the kind shown in Figure 1a in all possible ways; it is clear that there is a probability $1/k$ that the first particles will have the lowest index number as required, which leads to the following counting factor $f_{\text{diag.}}$ for pure exchange cycles:

$$f_{\text{diag.}} = \frac{1}{k} \quad (18)$$

⁽⁸⁾ There is some flexibility in this choice, and here we attempt to take the most convenient convention, but it is not necessarily the only possibility.

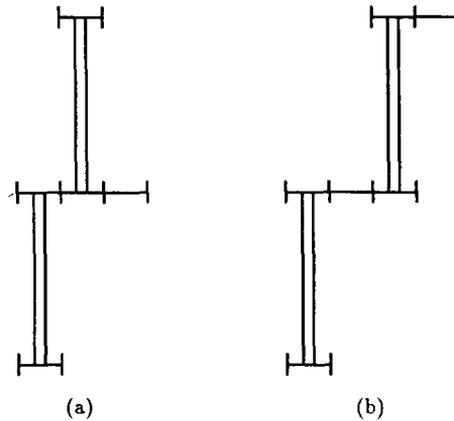


Fig. 2. — Other examples of U - C diagrams. As in Figure 1, horizontal lines correspond to exchange cycles containing U_1 operators; vertical double lines symbolize U_2 operators (triple lines would be used for U_3 , etc.). Formula (19) gives the weight of these diagrams; a more explicit calculation of these two terms is given in Appendix B.

(in other words, if one puts numbered particles into a cycle $C_k(.,.,.,.)$, one can obtain the same permutation k different times). Similarly, it is easy to see that the counting factors of the diagrams of Figures 1b and c are $1/2$, which corresponds to the probability of having the particle numbers contained inside the single U_2 in the correct order. The general value of counting factors is given in Appendix A; in many practical situations (when case (ii) of this Appendix does not occur) we can ignore the g 's in formula (A.1) and use the simpler form:

$$f_{\text{diag.}} = [p_{l_M} \times l_M]^{-1} \quad (19)$$

where l_M is the largest order of the Ursell operator contained in the diagram (one for Fig. 1a, two for Figs. b and c, three for Figs. 1d and e) while p_{l_M} is the number of these Ursell operators in this particular diagram (7 for Fig. 1a, one for all the other cases in this figure). Two other examples of diagrams for which this formula is valid are given in Figure 2; as an illustration, they are explicitly calculated in Appendix B.

We are now in a position to calculate $c\{m_{\text{diag.}}\}$. This number can be obtained by distributing the N particles within the sites of all the diagrams of a series defined by the m 's, which can be done in $N!$ different ways, and counting how many times the same term of the double summation of (11) is obtained. Since there are $m_{\text{diag.}}!$ ways to interchange the order of all U - C clusters arising from the same diagram, there is a first redundancy factor equal to $\prod_{\text{diag.}} (m_{\text{diag.}}!)$ that comes in. Moreover, there is also only a proportion $(f_{\text{diag.}})^{m_{\text{diag.}}}$ of the obtained configurations that is acceptable. Altogether, the net result is

$$c\{m_{\text{diag.}}\} = N! \prod_{\text{diag.}} \frac{1}{m_{\text{diag.}}!} [f_{\text{diag.}}]^{m_{\text{diag.}}} \quad (20)$$

3.2. TWO SUMMATIONS. — We now take advantage of the fact that (20) contains factorials and, in a second step, that the value of $f_{\text{diag.}}$ depends on the topology of the diagrams, but not on the size of the chains of U_1 's that it contains (except for pure exchange cycles). This

allows us to group together series of terms in (13). The first summation is done classically by going to the grand canonical ensemble and defining the corresponding partition function by:

$$Z_{g.c.} = \sum_N e^{\beta\mu N} Z_N \tag{21}$$

Then a useful simplification occurs because the sums over the $m_{diag.}$'s are now independent; moreover the factors $e^{\beta\mu N}$ can be reconstructed by multiplying every number $\Gamma_{diag.}$ by $e^{\beta\mu n_{diag.}}$, so that:

$$Z_{g.c.} = \prod_{diag.} \exp [\exp (\beta\mu n_{diag.}) \times f_{diag.} \times \Gamma_{diag.}] \tag{22}$$

We therefore obtain the grand potential (multiplied by $-\beta$) in the form:

$$\text{Log } Z_{g.c.} = \sum_{diag.} e^{\beta\mu n_{diag.}} \times f_{diag.} \times \Gamma_{diag.} \tag{23}$$

This is an exact formula, which gives the value of the pressure of the system (multiplied by its volume and divided by the temperature).

The second summation which can now be done consists in grouping together the contributions of all $U-C$ diagrams that have the same "frame" (or "skeleton"): we sum the diagrams which have the same topology and differ only, inside the horizontal lines that represent the permutation cycles, by the lengths of the intermediate chains of U_1 's that connect together the particles contained in the U_l 's with $l > 1$. Beside the fact that this operation turns out to be mathematically simple - it merely leads to the introduction of fractions of the operator U_1 as we will see in the next section (see also the discussion of Sect. 2 of Ref. [11]) -, it is also indispensable from a physical point of view: we have to make a summation over all lengths of intermediate horizontal chains of U_1 's in order to take into account an arbitrary degree of degeneracy. We call "classes" these groups of topologically equivalent $U-C$ diagrams; classes may also be represented by diagrams (Ξ -diagrams) which are, in a sense, simpler than the original diagrams since any indication of the length of the cycles has been removed. Examples are shown in Figure 3 where dashed lines mean that a summation over cycle length is implied. We call Ξ_{class} the contribution of a class; because the counting factors $f_{diag.}$ are equal for all diagrams of the same class ⁽⁹⁾, one can write:

$$\Xi_{class} = f_{class} \sum_{diag. \in class} e^{\beta\mu n_{diag.}} \times \Gamma_{diag.} \tag{24}$$

In terms of classes, (23) becomes:

$$\text{Log } Z_{g.c.} = \sum_{classes} \Xi_{class} \tag{25}$$

As (23), this is an exact formula, containing extensive quantities in both sides, and thus well adapted to approximations (as opposed to $Z_{g.c.}$ itself). We shall see below that the first term of the summation gives the grand potential ⁽¹⁰⁾ of an ideal, (degenerate), gas, which we shall note Ξ_{ideal} . The generalized Beth Uhlenbeck formula is contained in the second and the third term in the summation, which we shall note Ξ_{direct}^1 and $\Xi_{exch.}^1$, if, moreover, in each of these two classes, one limits the summation of (24) to its first term (lowest order in U_1), one recovers the usual formula, valid only for weakly degenerate gases.

⁽⁹⁾ Except for the ideal gas, which is a special case.

⁽¹⁰⁾ More precisely, the logarithms of partition functions give the value of the grand potential multiplied by $-\beta$.

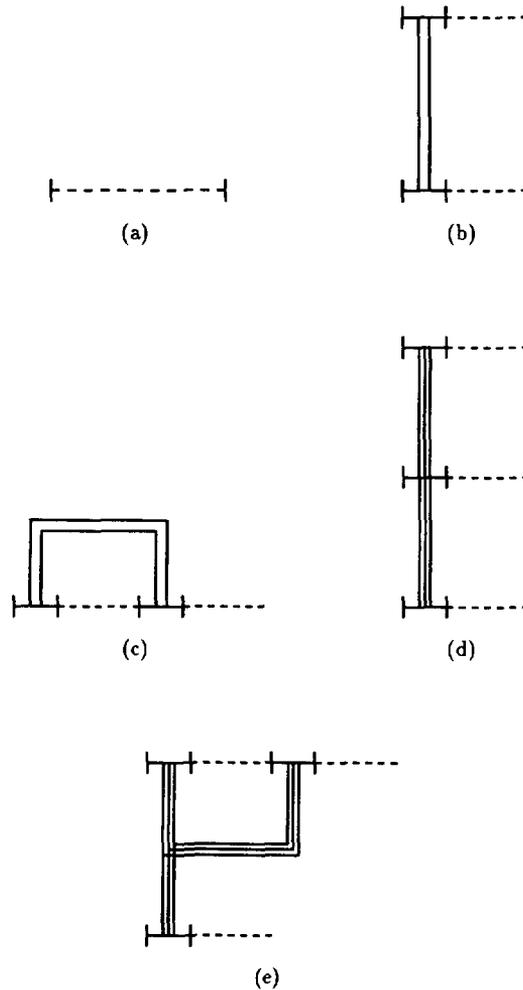


Fig. 3. — Ξ diagrams introduced by the summation of the diagrams of Figure 1 over the lengths of the U_1 chains, according to formula (24). The dashed lines, which symbolize these summations, can be replaced by intermediate operators given by fractions $1/[1 - \eta z U_1]$, where $z = \exp \beta \mu$; every operator U_l , with $l \geq 2$, remains explicit and, moreover, introduces a factor z^l ; finally, the weights f_{diag} must also be inserted in the value of the Ξ diagram.

4. Dilute Degenerate Systems

4.1. IDEAL GAS. — We first check that the first class of diagrams reconstructs the grand potential (multiplied by $-\beta$) of the ideal gas. This class, symbolized in Figure 3a, corresponds to the summation of the contribution of pure exchange cycles containing only U_1 's, summed over any length k ranging from one to infinity. We know from (18) the counting factor, so that we just need to calculate the numerical contribution Γ_k of every cycle. The result, proved below, is simple:

$$\Gamma_k = \eta^{k+1} \text{Tr} \left\{ [U_1]^k \right\} \quad (26)$$

where:

$$\eta = \begin{cases} 1 & \text{for bosons} \\ -1 & \text{for fermions} \end{cases} \tag{27}$$

This is again a consequence of the fact that the trace over the N particles contained in the diagram is taken in a space that is simply the tensor product of k single particle spaces of state. Because the numbering of the particles does not affect the value of Γ_k (it just changes the names of dummy variables), we can for convenience renumber the relevant particles from 1 to k . The effect of C_k is then to move particle 1 into the place initially occupied by particle 2, particle 2 into the place occupied by particle 3, and so on, until one comes back to the place of particle 1. Introducing a complete set of states $\{|\varphi_n\rangle\}$ in the one-particle space of states ⁽¹¹⁾, one can then write:

$$\begin{aligned} \Gamma_k &= \eta^{k+1} \sum_{n_1, n_2, \dots, n_k} \langle 1 : \varphi_{n_1} | U_1(1) | 1 : \varphi_{n_2} \rangle \langle 2 : \varphi_{n_2} | U_1(2) | 2 : \varphi_{n_3} \rangle \\ &\quad \times \dots \times \langle k : \varphi_{n_k} | U_1(k) | k : \varphi_{n_1} \rangle = \eta^{k+1} \text{Tr} \{ [U_1]^k \} \end{aligned} \tag{28}$$

(the factor η^{k+1} is equal to the parity of the cycle which enters the definition of A for fermions). We now have to make the summation:

$$\Xi_{\text{ideal}} = \sum_{k=1}^{\infty} \frac{1}{k} e^{\beta\mu k} \Gamma_k = \sum_{k=1}^{\infty} \frac{1}{k} e^{\beta\mu k} \eta^{k+1} \text{Tr} \{ [U_1]^k \} \tag{29}$$

which contains a well known series:

$$x + \eta \frac{x^2}{2} + \frac{x^3}{3} + \eta \frac{x^4}{4} + \dots = -\eta \text{Log} [1 - \eta x] \tag{30}$$

We therefore get for the grand potential (multiplied by $-\beta$) of the ideal gas:

$$\Xi_{\text{ideal}} = -\eta \text{Tr} \{ \text{Log} [1 - \eta e^{\beta\mu} U_1] \} \tag{31}$$

This is the classical result. For instance, we can assume that H_0 , the one-particle Hamiltonian, is equal to $P^2/2m$ (kinetic energy of a particle in a box); by replacing in (31) the trace by a sum over d^3k , and U_1 by its diagonal element $e^{-\beta\hbar^2 k^2/2m}$, one immediately recovers usual formulas that are found in most textbooks on statistical mechanics. Indeed, the method that we have used is more indirect than the traditional method, but it gives a physical interpretation to the term in $[U_1]^k$ that is obtained by expanding the logarithmic function of (31): it corresponds to the contribution of all possible cyclic exchanges of k particles in the system.

4.2. FIRST CORRECTION FOR SHORT RANGE POTENTIALS

4.2.1. *Correction to the Partition Function.* — What happens now if we add the two following terms in (25), which contain one single U_2 and no Ursell operator of higher order ? Let us start with the first class of diagrams, shown in figure 3b where the two particles in the U_2 operator belong to two different exchange cycles, and which we will call direct diagrams. In the first

⁽¹¹⁾ If the particles have internal states, the index n symbolizes at the same time the orbital quantum numbers as well as those characterizing the internal state. For instance, if the particles have spin I , a summation written as \sum_n contains in fact two summations, one over orbital quantum numbers, and a second over $(2I + 1)$ spin states.

diagram of this class, the two cycles are of length $k = 1$ (identities) and only two particles, unaffected by exchange, are involved; this simply introduces the contribution:

$$\Gamma_{11} = \text{Tr}_{1,2} \{U_2(1,2)\} \quad (32)$$

The next diagram in this class corresponds to three clustered particles, two contained in the same U_2 and two in one permutation operator C_2 . The numerical value of this second diagram is:

$$\begin{aligned} \Gamma_{2,1} &= \eta \text{Tr}_{1,2,3} \{U_2(1,2)U_1(3)C_2(1,3)C_1(2)\} \\ &= \eta \text{Tr}_{1,2,3} \{U_2(1,2)U_1(3)P_{\text{ex.}}(1,3)\} \end{aligned} \quad (33)$$

or:

$$\Gamma_{2,1} = \eta \sum_{n_1, n_2, n_3} \langle 1 : \varphi_{n_1} | \langle 2 : \varphi_{n_2} | U_2(1,2) | 1 : \varphi_{n_3} \rangle | 2 : \varphi_{n_2} \rangle \langle \varphi_{n_3} | U_1 | \varphi_{n_1} \rangle \quad (34)$$

which provides the following reduced value:

$$\Gamma_{2,1} = \eta \text{Tr}_{1,2} \{U_2(1,2)U_1(1)\} \quad (35)$$

Similarly, one would calculate a contribution $\Gamma_{1,2}$ arising from the exchange of particles 2 and 3, and obtained by replacing in (35) $U_1(1)$ by $U_1(2)$. More generally, when a U_2 operator clusters together k_1 particles, belonging to the same permutation cycle of length k_1 , with k_2 particles belonging to another cycle of length k_2 , the calculation of the effect of each of these cycles remains very similar to that of Section 4.1: now we have two particles that separately exchange with others, but the algebra of operators remains the same for each of them. We therefore get the reduced value:

$$\Gamma_{k_1, k_2} = \eta^{k_1-1} \eta^{k_2-1} \text{Tr}_{1,2} \left\{ U_2(1,2) [U_1(1)]^{k_1-1} [U_1(2)]^{k_2-1} \right\} \quad (36)$$

For this class of diagrams, according to (19) the counting factor f is simply 1/2. The last step is to make a summation over all possible values of k_1 and k_2 after inserting an exponential of β times the chemical potential multiplied by the number of particles contained in the diagram:

$$\Xi_{\text{direct}} = \frac{1}{2} \sum_{k_1, k_2} e^{\beta\mu(k_1+k_2)} \Gamma_{k_1, k_2} \quad (37)$$

This operation can be done by using the relation:

$$\sum_{k=1}^{\infty} (\eta x)^{k-1} = \frac{1}{1 - \eta x} \quad (38)$$

One therefore introduces fractions of the U_1 's operators, which results in the expression:

$$\Xi_{\text{direct}}^1 = \frac{1}{2} \text{Tr}_{1,2} \left\{ U_2(1,2) \frac{e^{\beta\mu}}{1 - \eta e^{\beta\mu} U_1(1)} \frac{e^{\beta\mu}}{1 - \eta e^{\beta\mu} U_1(2)} \right\} \quad (39)$$

For the second class of diagrams, exchange diagrams shown in Figure 3c, the two particles contained in U_2 are intermixed inside the same circular permutation. The first exchange diagram corresponds to the two particles contained in the same transposition:

$$\Gamma_{1,1}^{\text{ex}} = \text{Tr}_{1,2} \{U_2(1,2)\eta C_2(1,2)\} = \eta \text{Tr}_{1,2} \{U_2(1,2)P_{\text{ex.}}\} \quad (40)$$

The second contains three particles:

$$\Gamma_{1,2}^{\text{ex.}} = \text{Tr}_{1,2,3} \{U_2(1,2)U_1(3)C_3(1,2,3)\} \tag{41}$$

which is equal to:

$$\Gamma_{1,2}^{\text{ex.}} = \sum_{n_1, n_2, n_3} \langle 1 : \varphi_{n_1} | \langle 2 : \varphi_{n_2} | U_2(1,2) | 1 : \varphi_{n_2} \rangle | 2 : \varphi_{n_3} \rangle \langle \varphi_{n_3} | U_1 | 1 : \varphi_{n_1} \rangle \tag{42}$$

Now, we can use the equality:

$$\begin{aligned} \langle 1 : \varphi_{n_1} | \langle 2 : \varphi_{n_2} | U_2(1,2) | 1 : \varphi_{n_2} \rangle | 2 : \varphi_{n_3} \rangle &= \\ &= \langle 1 : \varphi_{n_1} | \langle 2 : \varphi_{n_2} | U_2(1,2)P_{\text{ex.}} | 1 : \varphi_{n_3} \rangle | 2 : \varphi_{n_2} \rangle \end{aligned} \tag{43}$$

which allows us to get the same summation over indices as in equation (34) and to obtain the reduced value:

$$\Gamma_{1,2}^{\text{ex.}} = \text{Tr}_{1,2} \{U_2(1,2)P_{\text{ex.}}U_1(1)\} \tag{44}$$

Another, very similar, term occurs if the circular permutation $C_3(1,2,3)$ of (41) is replaced by $C_3(1,3,2)$; the calculation can easily be repeated and provides the result:

$$\Gamma_{2,1}^{\text{ex.}} = \text{Tr}_{1,2} \{U_2(1,2)P_{\text{ex.}}U_1(2)\} \tag{45}$$

From the preceding equations it is not difficult to see that the generic term of this second class of diagrams is obtained from (36) by a simple replacement of U_2 by the product $\eta U_2 P_{\text{ex.}}$. Inserting a $P_{\text{ex.}}$ into (39) therefore provides $\Xi_{\text{exch.}}^1$. Finally, the value of the grand potential (multiplied by $-\beta$), to first order in U_2 , is given by:

$$\text{Log } Z_{\text{g.c.}} = \Xi_{\text{ideal}} + \text{Tr}_{1,2} \left\{ e^{2\beta\mu} U_2(1,2) \frac{[1 + \eta P_{\text{ex.}}]}{2} \frac{1}{1 - \eta e^{\beta\mu} U_1(1)} \frac{1}{1 - \eta e^{\beta\mu} U_1(2)} \right\} \tag{46}$$

This result is valid within an approximation which is basically a second virial treatment of the interactions, while it contains all statistical corrections. The formula remains therefore valid if the degree of degeneracy of the gas is significant. Nevertheless, as pointed out for instance in Section 2.1 of reference [12] and in reference [13], virial series (even summed to infinity) are no longer appropriate beyond values where the density exceeds that of a phase transition; this is because singularities in the thermodynamic quantities occur at a transition (in the limit of infinite systems). Therefore, for bosons, the validity of (46) is limited to non-condensed systems. The discussion of what happens when a Bose Einstein condensation takes place will be given in a future article

4.2.2. *Comparison with the Usual Beth Uhlenbeck Formula.* — We now show that equation (46) reduces to the Beth Uhlenbeck formula if the two denominators containing U_1 's are replaced by one, an operation which is valid in the limit of low densities where $e^{\beta\mu}$ is small. To see the equivalence between the low density limit of relation (46) with the usual value of the second virial correction, we start from the definition of the W_k functions given in equation (14.35) of reference [9], which for $k = 2$ becomes ⁽¹²⁾:

$$W_2(\mathbf{r}_1, \mathbf{r}_2) = 2(\lambda_T)^6 \sum_{n_s} | \Psi_{n_s}(\mathbf{r}_1, \mathbf{r}_2) |^2 e^{-\beta E_{n_s}} \tag{47}$$

⁽¹²⁾ We assume for simplicity that the particles have no internal state (or, if they do, that they are all in the same internal state).

where the functions $\Psi_{n_s}(\mathbf{r}_1, \mathbf{r}_2)$ are a complete set of stationary states for the system of identical particles (they are properly symmetrized); the thermal wavelength is defined by:

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} \quad (48)$$

Relation (47) can be transformed into:

$$W_2(\mathbf{r}_1, \mathbf{r}_2) = 2(\lambda_T)^6 \langle 1 : \mathbf{r}_1, 2 : \mathbf{r}_2 | \sum_{n_s} | \Psi_{n_s} \rangle \langle \Psi_{n_s} | e^{-\beta H} | 1 : \mathbf{r}_1, 2 : \mathbf{r}_2 \rangle \quad (49)$$

Inside this equation appears a closure summation over the symmetrized states of the system so that:

$$W_2(\mathbf{r}_1, \mathbf{r}_2) = 2(\lambda_T)^6 \langle 1 : \mathbf{r}_1, 2 : \mathbf{r}_2 | S e^{-\beta H} | 1 : \mathbf{r}_1, 2 : \mathbf{r}_2 \rangle \quad (50)$$

(for fermions, S is replaced by A). From this function reference [9] defines the Ursell function $U_2^H(\mathbf{r}_1, \mathbf{r}_2)$ by:

$$U_2^H(\mathbf{r}_1, \mathbf{r}_2) = W_2(\mathbf{r}_1, \mathbf{r}_2) - W_1(\mathbf{r}_1)W_1(\mathbf{r}_2) = \Delta W_2(\mathbf{r}_1, \mathbf{r}_2) + U_2^{\text{ideal gas}}(\mathbf{r}_1, \mathbf{r}_2) \quad (51)$$

where $\Delta W_2(\mathbf{r}_1, \mathbf{r}_2)$ is the difference between the values of $W_2(\mathbf{r}_1, \mathbf{r}_2)$ with and without interaction potential, and $U_2^{\text{ideal gas}}(\mathbf{r}_1, \mathbf{r}_2)$ the value of the Ursell function for a system of two free particles. Equation (14.49) ⁽¹³⁾ of [9] shows that the second virial coefficient in the expansion of the grand potential is half of the integral of $U_2^H(\mathbf{r}_1, \mathbf{r}_2)$ over the variables \mathbf{r}_1 and \mathbf{r}_2 , multiplied by $(\lambda_T)^{-3}$ and the inverse of the volume. But the contribution of $U_2^{\text{ideal gas}}(\mathbf{r}_1, \mathbf{r}_2)$ is automatically contained in $\text{Log } Z_{g.c.}$, so that we can concentrate on $\Delta W_2(\mathbf{r}_1, \mathbf{r}_2)$ only. Because the summation over \mathbf{r}_1 and \mathbf{r}_2 can be written as a trace in a space which is the tensor product of two one particle state spaces, and because:

$$S, A = \frac{1}{2} [1 \pm P_{ex}] \quad (52)$$

we get the result:

$$\int d^3 r_1 d^3 r_2 \Delta W_2^V(\mathbf{r}_1, \mathbf{r}_2) = 2(\lambda_T)^6 \text{Tr}_{1,2} \left\{ U_2(1, 2) \frac{[1 + \eta P_{ex.}]}{2} \right\} \quad (53)$$

where $U_2(1, 2)$ is the difference between the exponentials of the interacting particle Hamiltonian minus that of free particles, which is precisely our definition (3). We therefore recover our result (46), provided the denominators $1 - \eta e^{\beta \mu} U_1$ inside the trace are replaced by one.

4.2.3. *Discussion.* — The only difference between equation (46) and the Beth Uhlenbeck formula arises from the presence of the two fractions inside the trace. Since:

$$\frac{1}{1 - \eta e^{\beta \mu} U_1} = 1 + \eta \frac{e^{\beta \mu} U_1}{1 - \eta e^{\beta \mu} U_1} \quad (54)$$

they are actually nothing but operatorial forms of the usual Fermi or Bose factors $(1 + \eta f)$ that appear, for instance, in the collision term of the Uehling Uhlenbeck or Landau kinetic equation (with the usual notation f for the distribution function). In the present case, nevertheless, because U_2 and U_1 do not commute in general, the operatorial character of the fractions is relevant: in the absence of external potential (mutually interacting particles in a box) the

⁽¹³⁾ In the second edition, this equation is numbered (10.49).

eigenvectors of U_1 are plane waves (¹⁴), while those of U_2 are different since they involve correlations between the particles.

If the trace in the right hand side of (46) is calculated in the basis of plane waves, the correction is expressed as an integral containing the diagonal elements of U_2 between such plane waves. The simplest situation occurs when all these diagonal elements have the same sign. Then, for bosons, because the eigenvalues of the fractions are larger than 1, the effect of degeneracy is always to enhance the effects of interactions; this is physically satisfying since the Bose Einstein statistics tends to favor situations where particles are close. In particular, if the potential is attractive and if there are two body bound states (molecules), their weight will be increased with respect to what it would be in the usual Beth Uhlenbeck formula. If, on the other hand, the diagonal elements of U_2 between plane waves change sign when the relative momentum of the two particles changes, which may happen if the potential has attractive as well as repulsive parts, more complicated cancellation effects may take place in both the usual Beth Uhlenbeck formula and its generalization, so that no general prediction on the sign of the effect of degeneracy is possible (except for the contribution of bound states of bosons which remains enhanced as above).

For fermions, the eigenvalues of the fractions are between 0 and 1 so that the effect of statistics are just the opposite of what they are for bosons: they tend to reduce the effects of the interactions, except if mutual cancellation effects take place. Moreover, if the system is strongly degenerate, the effect of the product of the two fractions is to cancel the contribution of all matrix elements corresponding to particles inside the Fermi sphere, leaving only interactions between particles near the surface (or outside) of the Fermi sphere. This applies to bound molecules, which introduce a contribution containing the scalar product of the bound state wave function by all plane waves outside of the Fermi sphere, exactly as in the Cooper problem.

A final remark is related to the convergence of the power series that we have summed into fractions of the U_1 operators (the remark applies for fermions only). As noted by Kahn and Uhlenbeck [7], when the chemical potential of a system of fermions becomes positive, the virial series diverge, and the equation of state is obtained by a continuation of an analytic function. Here we observe the same phenomenon: the series in $[e^{\beta\mu}U_1]^k$ that we have summed over the size k of the exchange cycles becomes divergent when $\mu > 0$; nevertheless the sum remains a regular function and, for fermions, (46) has no singularity.

4.3. NEXT ORDER CORRECTION. — We now calculate further corrections to the partition function by including all diagrams containing two U_2 operators as well as those containing a single U_3 (and, of course, an arbitrary number of U_1 operators connected together by exchange cycles). We call their respective contributions to the logarithm of the partition function $\Xi_{(2 \times U_2)}$ and $\Xi_{(1 \times U_3)}$; the corresponding diagrams are shown in Figures 4 and 5.

4.3.1. *Diagrams Containing Two U_2 's.* — As shown in Figure 4, there are altogether ten diagrams containing two U_2 's; we note that, although for instance the diagrams (a) and (b) in this figure are topologically equivalent, they should indeed be considered as distinct; this is because the location of the starting point corresponding to the "base particle" (with our convention, that in the lowest left corner) is relevant according to our definition of diagrams; in the former the "base cycle" involves another U_2 operator, while in the second one it is the second exchange cycle which connects two U_2 's. The corresponding rules are explicitly given in Appendix A, Section (i).

(¹⁴) If the particles are subject to the effect of an external potential (atoms in a trap for instance), the eigenvectors of U_1 are not simple plane waves, but the essence of our analysis remains valid.

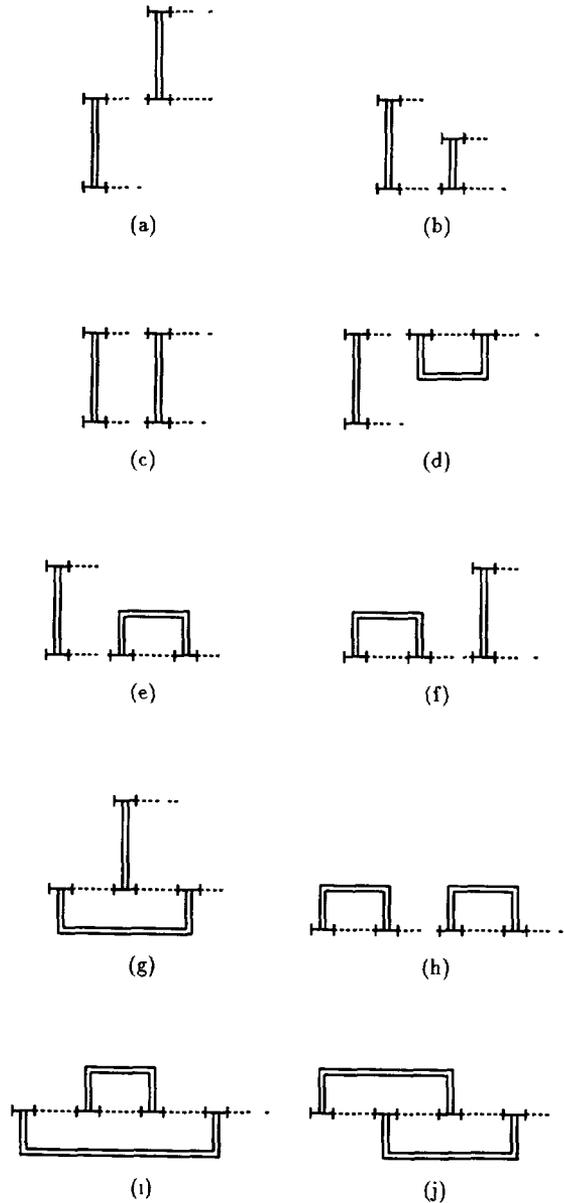


Fig. 4. — Diagrams containing two U_2 Ursell operators. All diagrams have the same counting factor $f_{\text{class}} = 1/4$. Diagrams (c) and (j) lead to a contribution proportional to a trace over the states of only two particles, whereas the expressions of the other diagrams are proportional to a trace over three particles.

The “reduced” contributions of these diagrams are relatively easy to calculate by using rules which can be inferred ⁽¹⁵⁾ from the calculations of the preceding section: (i) each extra

⁽¹⁵⁾ Alternatively, one can always come back to the “explicit” expression of diagrams, reduce the number of particles over which a trace is taken as was done for instance in (34) or (35), and check that the calculations are correct.

exchange cycle (horizontal line) introduces trace over a new particle, as well as a factor η ; (ii) dashed lines between two different U_2 operators, symbolizing summations over the length of U_1 -chains, introduce factors $(1 + \eta f)$ where the operator f and the fugacity z are defined by:

$$f = \frac{zU_1}{1 - \eta zU_1} \quad \text{and} \quad z = e^{\beta\mu} \quad (55)$$

In this way we obtain for the contributions of diagrams (a) and (b) the "reduced" expressions:

$$\eta \text{Tr}_{1,2,3} \{U_2(1, 2) [1 + \eta f(1)] [1 + \eta f(2)] U_2(2, 3) [1 + \eta f(2)] [1 + \eta f(3)]\} \quad (56)$$

and:

$$\eta \text{Tr}_{1,2,3} \{U_2(1, 2) [1 + \eta f(1)] [1 + \eta f(2)] U(1, 3) [1 + \eta f(1)] [1 + \eta f(3)]\} \quad (57)$$

The diagram noted (c) in Figure 4 involves only two distinct particles and yields:

$$\text{Tr}_{1,2} \left\{ [U_2(1, 2) [1 + \eta f(1)] [1 + \eta f(2)]]^2 \right\} \quad (58)$$

As in the previous section, a U_2 which connects two particles inside the same exchange cycle (a "closed U_2 ") leads to an expression where the U_2 is multiplied by an exchange operator ηP_{ex} , together with a trace over the "interior" particle. In other words, because the P_{ex} operator exchanges the two "legs" of the Ursell operator, the cycle of indices associated to the states of one given particle is now restricted to a part only of the horizontal line: when moving horizontally in the diagram, one has to skip the part of the line that is contained between the two legs; as for this part, it is separately closed under the effect of the P_{ex} operator, so that a trace over a different particle is introduced. For example we get for diagram (d):

$$\text{Tr}_{1,2,3} \{U_2(1, 2) [1 + \eta f(1)] [1 + \eta f(2)] U_2(2, 3) P_{ex}(2, 3) [1 + \eta f(2)] [1 + \eta f(3)]\} \quad (59)$$

Diagrams (e), (f) and (g) lead to expressions which differ only by the numbering of particles and are therefore equal; as for diagram (h), it gives the contribution:

$$\text{Tr}_{1,2,3} \{U_2(1, 2) P_{ex}(1, 2) [1 + \eta f(1)] [1 + \eta f(2)] U_2(2, 3) P_{ex}(2, 3) [1 + \eta f(2)] [1 + \eta f(3)]\} \quad (60)$$

while (i) is equal for the same reason.

The situation is slightly more complex for a "closed U_2 " operator when there is another U_2 operator which links a particle "inside" the U_2 with another particle of the same exchange cycle but "outside", as in diagram (j); in this case it turns out that no additional particle is needed. A calculation based either on the rules of the preceding paragraph, or starting from the "explicit expression" of this diagram, shows that its contribution is given by a trace over two particles only:

$$\text{Tr}_{1,2} \{U_2(1, 2) [1 + \eta f(1)] [1 + \eta f(2)] U_2(1, 2) P_{ex}(1, 2) [1 + \eta f(1)] [1 + \eta f(2)]\} \quad (61)$$

We then have to insert the counting factors f_{class} . In each diagram, U_2 is the highest order Ursell operator and there are two of them, so that according to formula (62) the counting factors are the same for all classes and are equal to $1/4$. Finally, using the fact that $U_2(1, 2)$ is invariant under exchange of particles 1 and 2 and that the numbering of particles inside the trace is irrelevant (dummy indices), we can write the complete contribution of all diagrams with two U_2 and an arbitrary number of U_1 operators in the form:

$$\begin{aligned} \Xi_{(2 \times U_2)} &= \frac{z^4}{2} \text{Tr}_{1,2} \left\{ \left[U_2^{S,A}(1, 2) [1 + \eta f(1)] [1 + \eta f(2)] \right]^2 \right\} \\ &\quad + 2\eta z^4 \text{Tr}_{1,2,3} \left\{ U_2^{S,A}(1, 2) [1 + \eta f(1)] [1 + \eta f(2)] \right. \\ &\quad \left. \times U_2^{S,A}(1, 3) [1 + \eta f(1)] [1 + \eta f(3)] \right\} \end{aligned} \quad (62)$$

where $U_2^{S,A}$ is defined as the symmetrized version of U_2 :

$$U_2^{S,A} = U_2 \frac{1 + \eta P_{ex}(1,2)}{2} \tag{63}$$

4.3.2. *Diagrams Containing a Single U_3 .* — The calculation of the contribution of all diagrams with one U_3 and an arbitrary number of U_1 operators is easier as there are only four diagrams and, moreover, there is only one U_l operator which involves more than one particle. Diagram (a) leads to a contribution proportional to:

$$\text{Tr}_{1,2,3} \{U_3(1,2,3) [1 + \eta f(1)] [1 + \eta f(2)] [1 + \eta f(3)]\} \tag{64}$$

Diagrams (b) and (c) introduce, in a way which is similar to what happened with “closed U_2 ” diagrams in the preceding section, an additional 2-particle exchange cycle P_{ex} multiplied by η . In diagram (d) we have a “completely closed U_3 ”, which yields, in an analogous manner, an U_3 multiplied by a 3-particle exchange cycle C_3 .

In the calculation of the counting factor f_{class} , the additional factor $(g)^{-1}$ (which is due to multiple connections) comes in for the first time (see Appendix A.(ii)). In diagram (a), we have to find the particle with the next-to-lowest index number among two exchange cycles in order to build up the diagram starting from the “base cycle”, while in diagram (b) we have to find this particle among two possible candidates of the same exchange cycle. Both cases

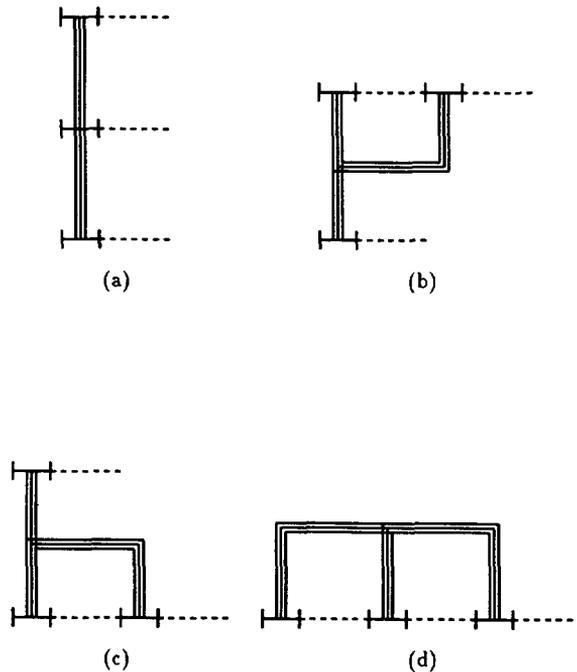


Fig. 5. — Diagrams containing one single U_3 Ursell operator. Diagrams (a) and (b) have counting factor $f_{class} = 1/6$ while (c) and (d) have $1/3$. Together with the particle exchange cycles appearing in the respective reduced expressions, these factors are precisely those that allow to group the three terms into a single final contribution which contains the symmetrizer (or antisymmetriser) of three particles.

result in $(g)^{-1} = 1/2$. In the last two diagrams there is no such ambivalence, so $(g)^{-1} = 1$. Furthermore there is a factor $(p_{l_M} \times l_M)^{-1} = 1/3$ which is common to all diagrams.

It turns out that these counting factors are exactly those necessary to reconstruct the 3-particle symmetrizer/antisymmetrizer S_3/A_3 (again using the fact that the indices in the trace are dummy). We thus obtain for the final contribution of all diagrams containing one U_3 operator:

$$\Xi_{(1 \times U_3)} = z^3 \text{Tr}_{1,2,3} \left\{ U_3^{S,A}(1, 2, 3) [1 + \eta f(1)] [1 + \eta f(2)] [1 + \eta f(3)] \right\} \quad (65)$$

where $U_3^{S,A}(1, 2, 3)$ is the symmetrized version of the three particle operator U_3 :

$$U_3^{S,A}(1, 2, 3) = U_3(1, 2, 3) \begin{matrix} S_3 \\ A_3 \end{matrix} \quad (66)$$

5. Discussion and Conclusion

A more detailed comparison between this work and other methods of approach can now be done. The basic idea of the method of Beth and Uhlenbeck, or more generally of Mayer cluster expansion methods [16], is to reason in terms of functions which directly give local approximations of the thermal equilibrium. Here we start from Ursell operators which give rise to various contributions in the form of U - C diagrams. This leads to equation (25) which provides an exact expression of the grand potential of the system, and expresses it as sum of various terms arising from Ξ -diagrams, already containing a sum over all possible sizes of intermediate exchange cycles. Each term is obtained as an integral (a trace) over a finite number of variables. The general expression is valid for dilute or dense systems as well, such as liquids or even solids; of course for gases it becomes simpler because it can be truncated more abruptly. Indeed, the generalization of the Beth Uhlenbeck formula is obtained by limiting the summation to the first three terms only (the first corresponding to the ideal gas).

The method that we have used is close to the "binary collision approximation" of Lee and Yang [14, 15]; these authors also introduce the Ursell functions of an auxiliary system obeying Boltzmann statistics, their aim being to establish relations between the Ursell functions of the two systems (see also Ref. [17] for a discussion of this type of method, as well as the article by Montroll and Ward [18]). Also, they introduce integrations over the inverse temperature to write their expansions, which is not done here. For these reasons, the similarity between the two methods is real but not obvious, either in the equations, or the diagrams, so that a close examination is necessary. Indeed, it is only after that a first version of the present article had been submitted for publication that the present authors realized that both methods can provide the same results: equation (II.8) of [14] is equivalent to equation (46), with different notation; in the same way, (II.18), (II.19) and (II.13) are equivalent to the results of Section 4.3. Nevertheless, the derivations remain rather different, mostly because we never introduce the Ursell functions of the system of indistinguishable particles in an intermediate step: we directly calculate the contributions of the Ursell operators of the auxiliary Boltzmann system to the grand potential by summing over the lengths of all exchange cycles. This may be the reason why our approach seems to be more compact and easier to handle, and allows writing calculations that are sometimes more general and explicit; in particular we give generic rules for obtaining the counting factors. In forthcoming articles we will exploit this relative simplicity to extend the application of our method beyond the only generalization of the Beth Uhlenbeck formula.

Probably the most popular method for handling interactions in quantum statistical mechanics is using perturbations expansions in terms of the interaction potential, at least as a starting

point, as for instance in the well known article of Bloch and De Dominicis [19]. By substituting the collision T matrix for the interaction potential, one can include in the final result an infinite number of terms of the expansion (resummation of ladder diagrams). The analogy with our method is that, as T , the second Ursell operator U_2 (or higher order operators) contain an infinite series of powers in the interaction potential. But the analogy remains limited: in our case, even at intermediate stage of the calculation, one never assumes that the potential is small (which technically avoids any divergence of the terms for hard core potential) and no replacement of V by T is necessary; actually T does not appear explicitly anywhere. The reason behind this difference is that the small parameter in our calculations is by no means the intensity of the potential, but its range b , which is physically a completely different quantity; this may be seen as a general difference between potential and density expansions.

In other words, the use of Ursell operators leads to a grouping of the terms of the usual expansion in terms of V that is different from what other approaches would provide. It extracts the terms that are actually dominant for a dilute gas, where only binary collision occur. For instance the corrections that are first order in b are entirely contained in the generalized Beth Uhlenbeck formula (46), which includes among others second order terms in V , while terms of the same order are also contained⁽¹⁶⁾ in the results obtained in Section 4.3; those are therefore contributions to the partition function that correspond to corrections in b of higher order. In a gas of many particles, second order terms in V may arise either from effects taking place within a single binary collision, or from the effect of two successive collisions involving one common particle carrying the information from one collision to the other. A second order calculation in V based on the formalism of the second quantization does not necessarily makes the difference between these two kinds of contributions. In our approach, on the other hand, the particles are indeed numbered at an intermediate stage⁽¹⁷⁾ and it is possible to keep track of "which particle is which", so that terms which are second order in V but negligible if b is small can be sorted out more easily.

Another interesting point of comparison is the more recent calculation by Nozières and Schmitt-Rink [20], who give a calculation of the thermodynamic potential for a system of fermions at low densities. In order to simplify the summation of the diagrams in their calculation, they assume that the matrix elements of the interaction potential are separable into a product of functions; moreover, for brevity, they explicitly include only one phase shift (s wave approximation) so that their result is less general than (46). Of course this does not mean that their method can not be generalized to fully recover (46), but we have not examined the question. In the same vein, a more detailed comparison between (46) with the results of Galitskii [6] for fermions and Belyaev [21] for bosons, valid at zero temperature, would be useful.

In an article in preparation, we show how the fact that our method fully includes the short range effect of the interaction potential on thermal equilibrium can be exploited for a precise study of the properties of the two body density operator, at short or long range, in particular to study the perturbation of the exchange hole of fermions (or bump for bosons) by a hard

⁽¹⁶⁾ The same remark holds for terms of higher order in V which, in our formalism, can be spread over a big variety of U - C diagrams, especially of course if the order is large.

⁽¹⁷⁾ This does not mean that statistics is not treated exactly in the final result; in fact, the effect of all exchange cycles is included without approximation in our calculations. For instance the fact that (46) is expressed mathematically as a trace over two numbered particles should not give the impression that it includes only exchange in a physical system of two particles only, such as a binary molecule: arbitrary long exchange cycles with an infinite number of particles are indeed included in the result. This is illustrated by the fact that (46) contains full Fermi Dirac or Bose Einstein distributions inside the degeneracy factors $[1 + \eta f]$. The limitation to exchange inside a binary system is rather a feature of the usual Beth Uhlenbeck theory.

core potential. Another article will contain a discussion of the description of Bose Einstein condensation and superfluidity in a dilute gas of bosons, and pairing in a dilute gas of fermions, as briefly sketched in the proceedings of a recent conference [11]. For the study of the phase transition corresponding to a divergence of the size of the dominant exchange cycles, it is natural to use a formalism where one keeps track of this size explicitly.

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Appendix A

General Rules for Constructing Diagrams

Our convention for building the diagram associated to any particular term in the double summation (9) is the following:

(i) we start from the U_l , or the U_l 's, that are of highest order $l = l_M$ in this particular term, and identify the particle it (or they) contain(s) that has the lowest index number n_{\min} ; this particle is considered as the "base particle", and belongs to the "base cycle" from which all the rest of diagram will be drawn. By convention, the base particle is shown first (left position) and the base cycle is that at the lowest position in the figure; for instance, in Figures 1b and 1d, this base is a three-particle cycle.

(ii) to continue in the construction of the diagram, we add a second generation of cycles. We first use the Ursell operator U_{l_M} that contains the base particle and add the other permutation cycles which include the other particles in the same U_{l_M} ; this is done in the order of increasing values for the index number of the particles contained in this U_{l_M} , so that the order of the new cycles is clearly defined. This also defines, for each of them, a "secondary base particle" that is put first in the diagram ⁽¹⁸⁾.

(iii) we continue the addition of this second generation of branches in the diagram by moving along the base cycle and skipping all numbered particles that are in U_l 's, until we reach one which belongs to an U_l with $l \geq 2$; we then add additional cycles containing the other particles inside this U_l . We use the same rule as in (ii) and we define "secondary bases" for the new cycles, so that their representation is also uniquely fixed. Going along all the base cycle in this way completes the first generation of additional cycles.

(iv) Then we build in the same way the second generation, by starting in succession from all of cycles of the first generation in the order in which they were added, etc. until, eventually, the complete diagram is obtained.

With these conventions, all cycles are individually identified, so that it makes sense to vary their lengths independently to generate all terms of (9); this will be useful below for the calculations which lead from the $U-C$ to the Ξ -diagrams. Figure 2 shows examples of diagrams;

⁽¹⁸⁾ If the connection is multiple, that is if the additional cycle contains several particles of the same base Ursell operator U_{l_M} , the secondary base particle is that of lowest index number; all the other particles are then automatically located in the diagram by their order in the exchange cycle, and do not play a special role at this stage.

Appendix B gives more details on the conventions used in their representation (in particular, it is convenient to assume that, inside the trace, the series of Ursell operators are put before the series of cycles).

Now suppose that we reverse the question: starting from a given diagram, how do we identify its occurrence in the double sum? what is its weight in the summation that gives $\text{Log } Z$? Assume that we throw randomly $n_{\text{diag.}}$ numbered particles into all available locations. With the precise rules that we have chosen above, it is clear that double counting problems are avoided, but also that not all of these random configurations obtained are allowed. What is the proportion $f_{\text{diag.}}$ of the configurations that are compatible with our conventions? Let us note p_{l_M} the total number of operators U_{l_M} (those of largest order l_M) appearing in this particular diagram. The reasoning is as follows:

- (i) first there is a probability $(p_{l_M} \times l_M)^{-1}$ that the right base particle will be obtained
- (ii) second, if $l_M \geq 3$, in the construction of successive generations of cycles, either more than one cycle is added from the connections of the same U_l , or there is a multiple connection towards the same cycle (or both). Figure 1e gives one example of such a multiple connection. In all these cases, additional factors $(g)^{-1}$ are introduced which account for the correct ordering of numbering of secondary base particles.

Thus we obtain:

$$f_{\text{diag.}} = [p_{l_M} \times l_M \times g]^{-1} \quad (\text{A.1})$$

(this formula is also valid if $l_M = 1$, in which case p_{l_M} is nothing but the size k of the linear exchange cycle). For the generalization of the Beth Uhlenbeck formula, case (ii) never happens and the factors g 's do not play any role; they nevertheless enter the calculations of Section 4.3.

Appendix B

Two Examples

The diagram shown in Figure 2a corresponds by definition to the following trace:

$$\text{Tr}_{1,2,3,4,5} \{U_2(1,2)U_2(3,5)U_1(4)C_1(1)C_3(2,3,4)C_1(5)\} \quad (\text{B.1})$$

Our convention is that the Ursell operators are always put before the cycles; the notation $C_3(2,3,4)$ refers to a cycle where the particle numbered 2 replaces that numbered 3, that numbered 3 replaces that numbered 4, and that numbered 4 that numbered 2 (the C_1 's do not produce any change in the positions of the particles). Equation (B.1) gives what we call the "explicit value" of this particular diagram, but it can also be simplified into a "reduced value". This can be done by inserting into (B.1) closure relationships and using summations to introduce products of operators whenever possible. In this case this leads to the expression:

$$\text{Tr}_{1,2,5} \{U_2(1,2)U_2(2,5)U_1(2)\} \quad (\text{B.2})$$

In the explicit value, any numbered particle appears once and only once in every Ursell operator and every cycle; in the reduced form this is not necessarily the case.

In a similar way the diagram shown in Figure 2b is defined by the explicit expression:

$$\text{Tr}_{1,2,3,4,5,6} \{U_2(1,2)U_1(3)U_2(4,5)U_1(6)C_1(1)C_3(2,3,4)\eta C_2(5,6)\} \quad (\text{B.3})$$

while its reduced value is:

$$\eta \text{Tr}_{1,2,5} \{U_2(1,2)U_1(2)U_2(2,5)U_1(5)\} \quad (\text{B.4})$$

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