

Many-Body Problem in Quantum Statistical Mechanics. IV. Formulation in Terms of Average Occupation Number in Momentum Space*

T. D. LEE, *Columbia University, New York, New York*

AND

C. N. YANG, *Institute for Advanced Study, Princeton, New Jersey*

(Received June 26, 1959)

Starting from Rules *A* and *B* of a previous paper (I), it is shown that the grand partition function can be evaluated in terms of the statistical averages of the occupation number in momentum space. The final formulation is in terms of a simple variational principle. The procedure represents a concise and complete separation of the effect of the Bose-Einstein or Fermi-Dirac statistical character of the particles from the dynamical problem. In the case of Bose statistics, this formulation makes possible a systematic computation of all thermodynamic functions near the Bose-Einstein transition point in the gaseous phase. Applications to a system of hard spheres are discussed.

1. INTRODUCTION

IN paper I¹ of the present series it was shown that the thermodynamical functions for a quantum mechanical system of particles obeying the symmetrical or anti-symmetrical statistics can be computed from a knowledge of certain U_l functions for the same system obeying Boltzmann statistics. The method of computation was called Rule *A* and Rule *B* which embody the influence of statistics on the thermodynamical functions. The dynamical part of the problem is embodied, on the other hand, in the functions U_l .

The purpose of this paper² is to analyze further the effects of statistics in a system of interacting particles. It is found that the thermodynamical functions can be expressed explicitly in terms of the statistical averages $\langle n_k \rangle$ of the occupation numbers in momentum space. Furthermore, the procedures of calculation are concisely formulated without approximations as variational principles.

In the case of Bose statistics, this new formulation is also physically necessary to make possible a general treatment of the Bose-Einstein transition problems which will be discussed in detail in the subsequent paper (paper V).

It is generally accepted that the λ -transition in liquid He is due to the Bose statistical nature of the atoms. In fact it is natural to conjecture that the transition is caused by some peculiar properties of the average occupation number $\langle n_k \rangle$ at $k=0$. However, attempts at a systematic treatment of the problem have always

been obstructed by the complicated dynamical problem involved. The present formalism, in separating out the statistics property from the dynamical property of a system and in using the average occupation numbers $\langle n_k \rangle$ as a primary concept in the analysis, offers new possibilities for a more complete understanding of transitions that are of purely statistical origin.

In Secs. 2 to 8 we give the general developments for the case of Bose statistics. Applications to a Bose system of hard spheres are discussed in Secs. 9 and 10. The corresponding developments for Fermi statistics are given in Sec. 11.

2. GRAND PARTITION FUNCTION (BOSE STATISTICS)

We consider a system of interacting Bose particles in a finite volume Ω . The grand partition function \mathcal{Q}_Ω^S is related to the functions U_l^S by [see Eq. (I.13) of paper I]

$$\ln \mathcal{Q}_\Omega^S = \sum_{l=1}^{\infty} (l!)^{-1} z^l \sum_{\mathbf{k}_1 \dots \mathbf{k}_l} \langle \mathbf{k}_1, \dots, \mathbf{k}_l | U_l^S | \mathbf{k}_1, \dots, \mathbf{k}_l \rangle. \quad (\text{IV.1})$$

These U_l^S can be computed in terms of U_l through Rule *A* of paper I. As mentioned in I, in this computation instead of U_l only the symmetric combination Υ_l^S occurs, where Υ_l^S is defined by [see Eq. (I.30)]

$$\begin{aligned} & \langle \mathbf{k}_1', \mathbf{k}_2', \dots, \mathbf{k}_l' | \Upsilon_l^S | \mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_l \rangle \\ & \equiv \sum_{P'} P' \langle \mathbf{k}_1', \mathbf{k}_2', \dots, \mathbf{k}_l' | U_l | \mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_l \rangle. \end{aligned} \quad (\text{IV.2})$$

In (IV.2) the sum extends over all $l!$ permutations of $\mathbf{k}_1', \mathbf{k}_2', \dots, \mathbf{k}_l'$. Thus we may state Rule *A* in a slightly altered form as follows:

Rule *A'*.—To calculate $\langle \mathbf{k}_1' \mathbf{k}_2' \dots \mathbf{k}_l' | U_l^S | \mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_l \rangle$ we first consider a grouping of the l integers $1, \dots, l$

$$\{(a)(b) \dots\} \{(cd)(ef) \dots\} \{(ghi) \dots\} \dots \quad (\text{IV.3})$$

where $ab \dots cdef \dots ghi \dots$ is a permutation of these l integers. In the first curly bracket there are m_1 round brackets with one integer in each ($m_1=0, 1, 2, \dots$) and

* Work supported in part by the U. S. Atomic Energy Commission.

¹ T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1165 (1959), hereafter referred to as I. Throughout this paper we use the same notations as I.

² It may be remarked that the contents of this and the subsequent papers (IV and V) depend only on the general methods discussed in I. The discussions in II and III [T. D. Lee and C. N. Yang, Phys. Rev. **116**, 25 (1959); **117**, 12 (1960)] represent some other parallel developments and applications which are not necessary for an understanding of the present paper. The reader is also referred to M. S. Green, Phys. Rev. Letters **1**, 409 (1958) for a parallel discussion of the problems treated in the present paper.

in the second curly bracket there are m_2 round brackets with two integers in each ($m_2=0, 1, 2, \dots$), etc.

$$\sum_{\alpha} m_{\alpha} \alpha = l.$$

Within each round bracket the integers are arranged in ascending order and within each curly bracket the round brackets are so arranged such that their first integers follow an ascending sequence. We then form the sum

$$\sum \{ \langle \mathbf{k}_A' | \Upsilon_1^S | \mathbf{k}_a \rangle \langle \mathbf{k}_B' | \Upsilon_1^S | \mathbf{k}_b \rangle \dots \} \times \{ \langle \mathbf{k}_C', \mathbf{k}_D' | \Upsilon_2^S | \mathbf{k}_c, \mathbf{k}_d \rangle \dots \} \dots, \quad (\text{IV.4})$$

where $AB \dots CD \dots$ is a permutation of $1, 2, \dots$. Because we use Υ_i^S in (IV.3), among all the permutations $AB \dots CD \dots$ which differ from each other *only* in the relative positions of numbers *within the same bra* (e.g., $\langle \mathbf{k}_C', \mathbf{k}_D' |$ and $\langle \mathbf{k}_D', \mathbf{k}_C' |$) only one such permutation will be included in the sum (IV.4). The sum (IV.4) then extends over all permutations provided further that upon setting $\mathbf{k}_i' = \mathbf{k}_i$ (for all i) the summand in (IV.4) cannot be written as a product of two factors, one of which depends only on some, but not all, of the coordinates $\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_l$ while the other depends only on the rest of these coordinates. The sum of all expressions (IV.4) over the different groupings (IV.3) then gives $\langle \mathbf{k}_1' \dots \mathbf{k}_l' | \Upsilon_l^S | \mathbf{k}_1 \dots \mathbf{k}_l \rangle$.

We give a few examples³ of Rule A' .

Example (1):

$$\langle \mathbf{k}' | \Upsilon_1^S | \mathbf{k} \rangle = \langle \mathbf{k}' | \Upsilon_1^S | \mathbf{k} \rangle = \langle \mathbf{k}' | \Upsilon_1 | \mathbf{k} \rangle = \delta_{\mathbf{k}\mathbf{k}'} \exp(-\beta \mathbf{k}^2). \quad (\text{IV.5})$$

Example (2):

$$\langle 1', 2' | \Upsilon_2^S | 1, 2 \rangle = \langle 2' | \Upsilon_1 | 1 \rangle \langle 1' | \Upsilon_1 | 2 \rangle + \langle 1', 2' | \Upsilon_2^S | 1, 2 \rangle. \quad (\text{IV.6})$$

Example (3):

$$\begin{aligned} \langle 1', 2', 3' | \Upsilon_3^S | 1, 2, 3 \rangle &= \langle 1' | \Upsilon_1 | 3 \rangle \langle 3' | \Upsilon_1 | 2 \rangle \langle 2' | \Upsilon_1 | 1 \rangle \\ &+ \langle 1' | \Upsilon_1 | 2 \rangle \langle 2' | \Upsilon_1 | 3 \rangle \langle 3' | \Upsilon_1 | 1 \rangle \\ &+ \langle 2' | \Upsilon_1 | 3 \rangle \langle 1', 3' | \Upsilon_2^S | 1, 2 \rangle \\ &+ \langle 3' | \Upsilon_1 | 2 \rangle \langle 1', 2' | \Upsilon_2^S | 1, 3 \rangle \\ &+ \langle 1' | \Upsilon_1 | 3 \rangle \langle 2', 3' | \Upsilon_2^S | 1, 2 \rangle \\ &+ \langle 3' | \Upsilon_1 | 1 \rangle \langle 1', 2' | \Upsilon_2^S | 2, 3 \rangle \\ &+ \langle 1' | \Upsilon_1 | 2 \rangle \langle 2', 3' | \Upsilon_2^S | 1, 3 \rangle \\ &+ \langle 2' | \Upsilon_1 | 1 \rangle \langle 1', 3' | \Upsilon_2^S | 2, 3 \rangle \\ &+ \langle 1', 2', 3' | \Upsilon_3^S | 1, 2, 3 \rangle. \quad (\text{IV.7}) \end{aligned}$$

3. PRIMARY GRAPHS (BOSE STATISTICS)

By using (IV.1) and Rule A' , the logarithm of the grand partition function can be expressed as a sum over expressions (IV.4). It is useful to represent each of these terms in (IV.4) graphically. Indeed, a major part of the discussions in this paper is just to find a con-

³ For simplicity, we use $1\ 2\ 3 \dots$ and $1'\ 2'\ 3' \dots$ to represent $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3 \dots$ and $\mathbf{k}_1', \mathbf{k}_2', \mathbf{k}_3' \dots$, respectively.

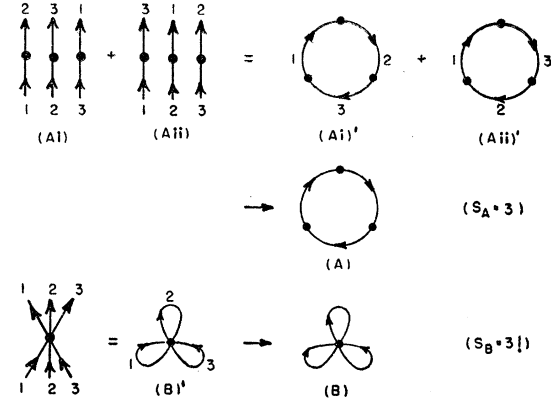


FIG. 1. Evolutions from diagrams to primary graphs. (A) and (B) are primary 0-graphs.

venient way of representing these sums by appropriate graphs. For clarity, we shall present the gradual evolutions and successive simplifications of these graphical methods instead of immediately presenting the final rules.

As an example, let us first consider two specific terms (Ai) and (Aii) in (IV.4),

$$(Ai) = \langle 2 | \Upsilon_1 | 1 \rangle \langle 3 | \Upsilon_1 | 2 \rangle \langle 1 | \Upsilon_1 | 3 \rangle, \quad (\text{IV.8})$$

$$(Aii) = \langle 3 | \Upsilon_1 | 1 \rangle \langle 1 | \Upsilon_1 | 2 \rangle \langle 2 | \Upsilon_1 | 3 \rangle. \quad (\text{IV.9})$$

In Fig. 1 we represent (Ai) by a diagram in which the three incoming (i.e., with their directions pointing towards the vertex points) lines 1, 2, 3 represent, respectively, the three kets $|1\rangle$, $|2\rangle$, and $|3\rangle$ in (IV.8); the three outgoing (i.e., with their directions pointing away from the vertex points) lines 1, 2, 3 represent the corresponding three bras $\langle 1|$, $\langle 2|$, and $\langle 3|$. These lines are connected at various vertex points that correspond to the Υ_1 factors in (IV.8). In a similar way, we represent the term (Aii) by a diagram in Fig. 1. Next, to show the connectivity of these diagrams, we connect, respectively, the incoming lines 1, 2, 3 with the outgoing lines 1, 2, 3. The resulting diagrams are shown as $(Ai)'$ and $(Aii)'$ in Fig. 1. Since in (IV.1) $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3$ are to be summed over, both (Ai) and (Aii) give identical contributions to the sum (IV.1) for $\ln \mathcal{Q}_\Omega^S$. It is therefore convenient to omit the numbers 1, 2, 3 from these diagrams and represent both terms by a single graphical structure, called a *primary graph* (or, primary 0-graph), which is shown as A in Fig. 1.

Next, as another example, we consider some other terms in (IV.4), e.g.,

$$\langle 1, 2, 3 | \Upsilon_3^S | 1, 2, 3 \rangle. \quad (\text{IV.10})$$

Again we first represent the ket $|1, 2, 3\rangle$ by three incoming lines 1, 2, 3 and the bra $\langle 1, 2, 3|$ by three outgoing lines 1, 2, 3. These lines are connected at a vertex point which corresponds to Υ_3^S . We then connect the incoming lines 1, 2, 3, respectively with their corresponding outgoing lines. Finally, we omit these numbers

1, 2, 3 and obtain a primary graph B which is also shown in Fig. 1. Unlike the previous example where the primary graph A represents the sum of the contributions of two terms (Ai) and (Aii) to (IV.1), the primary graph B represents only the contribution of a single term (IV.10).

In an entirely similar way we may represent $\ln \mathcal{Q}_\alpha^S$ as a sum over various primary graphs.

We define a *primary graph* to be a single (i.e., all parts being connected) graphical structure which must contain at least one line and at least one vertex. These lines are connected with each other at various vertices. Each line has a direction indicated by an arrow. Each vertex, called α -vertex, connects α incoming (i.e., with their directions towards the vertex) lines and α outgoing (i.e., with their directions away from the vertex) lines. A line which has vertices at both ends is called an internal line; otherwise, it is called an external line. All external lines are considered distinguishable and different. Two primary graphs are different if their topological structures are different. For example, the length and curvature of each line are completely unspecified and immaterial.

A *primary ζ -graph* ($\zeta=0, 1, 2, \dots$) is a primary graph which has ζ external incoming lines and ζ external outgoing lines. It is clear that to express $\ln \mathcal{Q}_\alpha^S$ we need only the special case $\zeta=0$. Higher ζ values will be important for computing other physical quantities.

To each primary ζ -graphs we assign a term which is determined by the following procedures:

(i) Associate with each internal line a different integer i ($i=1, 2, \dots, l$) and a corresponding momentum \mathbf{k}_i .

(ii) If $\zeta \neq 0$, then associate the external lines with certain pre-given momenta.

(iii) To each α -vertex, assign a factor

$$\langle \mathbf{k}_{B1} \dots \mathbf{k}_{B\alpha} | \Upsilon_\alpha^S | \mathbf{k}_{A1} \dots \mathbf{k}_{A\alpha} \rangle,$$

where $\mathbf{k}_{A1} \dots \mathbf{k}_{A\alpha}$ are the momenta associated with its incoming (internal or external) lines and $\mathbf{k}_{B1} \dots \mathbf{k}_{B\alpha}$ are the momenta associated with its outgoing (internal or external) lines.

(iv) Assign a factor z to each *internal* line.

(v) Assign a factor S^{-1} to the entire graph where

$$S = \text{symmetry number} \quad (\text{IV.11})$$

and is defined as follows:

Consider all $l!$ permutations of the positions of the l integers associated with the internal lines. The total number of permutations that leave the graph topologically (including the relative positions of these numbers 1, 2, \dots, l) unchanged is called the symmetry number of the graph.⁴ (Some examples of symmetry numbers are given in Fig. 2.)

⁴ Let us consider the two primary graphs (A) and (B) in Fig. 1 and denote their symmetry numbers by S_A and S_B , respectively. We follow step (i). These two primary graphs become, say, $(Ai)'$ and $(B)'$, respectively. For $(B)'$, all the $3!$ permutations of $(1\ 2\ 3)$

The term that corresponds to each graph is given by

$$\sum_{\mathbf{k}_1 \dots \mathbf{k}_l} [\text{product of all factors in (iii)-(v)}]. \quad (\text{IV.12})$$

In terms of these primary graphs we can write the sum (IV.1) as (proved in Appendix A)

$$\ln \mathcal{Q}_\alpha^S = \sum (\text{all different primary 0-graphs}) \quad (\text{IV.13})$$

in which each graph contributes a term given by (IV.12).

The sum (IV.13) is illustrated in Fig. 3. More explicitly, one can write (IV.13) as

$$\begin{aligned} \ln \mathcal{Q}_\alpha^S = & \sum_{\mathbf{k}} [z \exp(-\beta \mathbf{k}^2) \\ & + \frac{1}{2} z^2 \exp(-2\beta \mathbf{k}^2) + \frac{1}{3} z^3 \exp(-2\beta \mathbf{k}^2) + \dots] \\ & + \sum_{\mathbf{k}_1 \mathbf{k}_2} \langle \mathbf{k}_1 \mathbf{k}_2 | \Upsilon_2^S | \mathbf{k}_1 \mathbf{k}_2 \rangle \{ \frac{1}{2} z^2 + z^3 \exp(-\beta \mathbf{k}_1^2) \\ & + \frac{1}{2} z^4 \exp[-\beta(\mathbf{k}_1^2 + \mathbf{k}_2^2)] + \dots \} \\ & + \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3} \langle \mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3 | \Upsilon_3^S | \mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3 \rangle \\ & \times [\frac{1}{6} z^3 + \frac{1}{2} z^4 \exp(-\beta \mathbf{k}_1^2) + \dots] + \dots, \quad (\text{IV.14}) \end{aligned}$$

in which each term in the sum corresponds to the primary 0-graph at the corresponding position in the

S_0	A	B	S_1	n
2			1	2
8			2	4
6			2	3
4			2	2
			2	2
			4	1

FIG. 2. Relationship between irreducible 0-graphs and irreducible 1-graphs. The derivative with respect to $M(\mathbf{k})$ of an irreducible 0-graph listed in column A is the sum of the corresponding irreducible 1-graphs listed in column B . The number n is the number of lines in the 0-graph, which, when cut, gives rise to the 1-graph. Notice that Eq. (IV.103) is satisfied in every case.

leave its topological structure (including the relative positions of 1, 2 and 3) unchanged. Thus $S_B=3!$. For $(Ai)'$ only the cyclic permutations $\begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix}$, $\begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix}$, and $\begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix}$ leave the topological positions of these numbers unchanged. Thus, $S_A=3$.

sum in Fig. 3. In (IV.14) we have used the explicit form of U_1 given by (IV.5).

4. CONTRACTED GRAPHS (BOSE STATISTICS)

In Fig. 3 we have arranged the sum so that the different primary graphs in the same row have the same number of α -vertices for $\alpha \geq 2$ but differ *only* in the total number and relative positions of 1-vertices. Because of (IV.5), we see that all the terms in the same row in (IV.14) can be easily summed over. Thus (IV.14) becomes

$$\begin{aligned} \ln \mathcal{Q}_\Omega^S = & \sum_{\mathbf{k}} \ln [z^{-1} m(\mathbf{k})] \\ & + \frac{1}{2} \sum_{\mathbf{k}_1 \mathbf{k}_2} \langle \mathbf{k}_1 \mathbf{k}_2 | \Upsilon_2^S | \mathbf{k}_1 \mathbf{k}_2 \rangle m(\mathbf{k}_1) m(\mathbf{k}_2) \\ & + \frac{1}{6} \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3} \langle \mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3 | \Upsilon_3^S | \mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3 \rangle \\ & \times \prod_{i=1}^3 m(\mathbf{k}_i) + \dots, \quad (\text{IV.15}) \end{aligned}$$

where

$$m(\mathbf{k}) = z[1 - z \exp(-\beta \mathbf{k}^2)]^{-1}. \quad (\text{IV.16})$$

It is therefore convenient to represent the primary graphs in the same row in Fig. 3 by a single structure which is obtained from any one of these primary graphs by simply deleting all 1-vertices.

We now introduce the definition of a contracted graph. A *contracted graph* (or, contracted ζ -graph) has

$$\begin{aligned} \ln \mathcal{Q}_\Omega^S = & \text{(1)} + \text{(2)} + \text{(3)} + \dots \\ & + \text{(2)} + \text{(1)} + \text{(2)} + \dots \\ & + \text{(3!)} + \text{(2)} + \dots \\ & + \text{(2)} + \text{(1)} + \dots \\ & + \dots \\ = & \sum_{\mathbf{k}} \ln [z^{-1} m(\mathbf{k})] + \text{(2)} + \text{(3!)} \\ & + \text{(2)} + \dots \end{aligned}$$

FIG. 3. $\ln \mathcal{Q}_\Omega^S$ as a sum over different primary 0-graphs and as a sum over different contracted 0-graphs. Solid lines are for primary graphs and the dotted lines are for contracted graphs. The symmetry numbers are listed under the graphs.

the same topological structure as a primary graph (or, primary ζ -graph) except that a contracted graph *does not have any 1-vertices*. To each contracted graph we assign a term which is determined by the same procedures (i)–(v) used to obtain (IV.12), except that (iv) is replaced by

(iv)' Assign a factor $m(\mathbf{k}_i)$ to the i th *internal* line ($i=1, 2, \dots, l$).

The term that corresponds to a contracted graph is then given by

$$\sum_{\mathbf{k}_1 \dots \mathbf{k}_l} [\text{product of all factors in (iii), (iv)', and (v)}]. \quad (\text{IV.17})$$

In terms of these contracted graphs (IV.13) becomes⁵

$$\ln \mathcal{Q}_\Omega^S = \sum_{\mathbf{k}} \ln [z^{-1} m(\mathbf{k})] + \sum (\text{all different contracted 0-graphs}). \quad (\text{IV.18})$$

This sum is also illustrated in Fig. 3 in which, for the sake of clarity, solid lines are used for the primary graphs and dotted lines are used for the contracted graphs. It is important to notice that the role of symmetry numbers is preserved under this process of contraction.

The first few terms in the sum (IV.18) have also been derived in paper II.⁶

At $z=1$, $m(\mathbf{k})$ has a singularity at $\mathbf{k}=0$. The summation (IV.18) therefore is useful only for $z < 1$. As was pointed out in a previous paper,⁷ for a system of dilute Bose hard spheres the thermodynamical functions do not have a singularity at $z=1$. In fact, through a rearrangement of the virial expansions the actual phase transition was found to occur at $z > 1$.

It will be shown in Sec. 6 that mathematically such rearrangement processes are identical with the study of the reducibility of the graphs. To see this and to extend these results to a general system of interacting bosons, it is useful to discuss first some properties between graphs and the average occupation numbers in momentum space.

5. AVERAGE OCCUPATION NUMBER IN MOMENTUM SPACE AND $M(\mathbf{k})$ (BOSE STATISTICS)

We define $\langle n_{\mathbf{k}} \rangle$ to be the statistical value of the number of particles⁸ with a definite momentum \mathbf{k} in a finite volume, averaged over the grand canonical ensemble. These average numbers can be shown to be

⁵ For the sake of uniformity we choose the definition that every graph (primary, contracted or irreducible) must contain at least one vertex. Thus, if we delete all 1-vertices from any primary graph in the first row in Fig. 3 the result is *not* a contracted graph.

⁶ T. D. Lee and C. N. Yang, Phys. Rev. **116**, 25 (1959), hereafter referred to as II.

⁷ T. D. Lee and C. N. Yang, Phys. Rev. **112**, 1419 (1958). See especially the discussions given in Sec. 8.

⁸ $\langle n_{\mathbf{k}} \rangle$ is the occupation number for particles, not the so-called phonons.

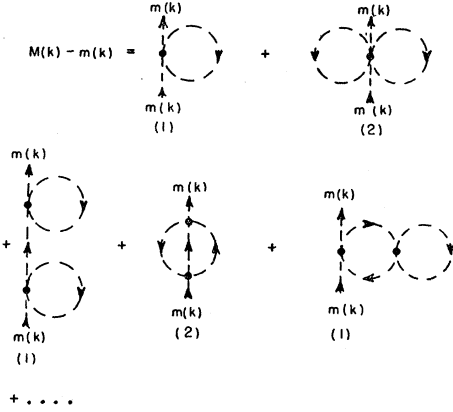


FIG. 4. $[M(\mathbf{k}) - m(\mathbf{k})]$ as a sum over different contracted 1-graphs. The corresponding symmetry numbers are listed under the graphs. Each graph contributes a term equal to (IV.17) times $m^2(\mathbf{k})$. [See reference 9.]

related to U_l^S by (to be proved in Appendix B)

$$\langle n_k \rangle = \sum_{l=1}^{\infty} [(l-1)!]^{-1} z^l \times \sum_{\mathbf{k}_1 \dots \mathbf{k}_{l-1}} \langle \mathbf{k}_1, \dots, \mathbf{k}_{l-1}, \mathbf{k} | U_l^S | \mathbf{k}_1, \dots, \mathbf{k}_{l-1}, \mathbf{k} \rangle. \quad (\text{IV.19})$$

For reasons which will become clear later, it is extremely useful to define a function $M(\mathbf{k})$ related to $\langle n_k \rangle$ by

$$M(\mathbf{k}) \equiv z[\langle n_k \rangle + 1]. \quad (\text{IV.20})$$

By using (IV.19), $M(\mathbf{k})$ can be written as

$$M(\mathbf{k}) = z + z^2 \left[\sum_{l=0}^{\infty} (l!)^{-1} z^l \times \sum_{\mathbf{k}_1 \dots \mathbf{k}_l} \langle \mathbf{k}_1, \dots, \mathbf{k}_l | U_{l+1}^S | \mathbf{k}_1, \dots, \mathbf{k}_l, \mathbf{k} \rangle \right]. \quad (\text{IV.21})$$

The function $M(\mathbf{k})$ is related to the grand partition function \mathcal{Q}_Ω^S by

$$\sum_{\mathbf{k}} [z^{-1} M(\mathbf{k}) - 1] = \sum_{\mathbf{k}} \langle n_k \rangle = z \frac{\partial}{\partial z} \ln \mathcal{Q}_\Omega^S. \quad (\text{IV.22})$$

By using Rule A', $M(\mathbf{k})$ and $\langle n_k \rangle$ can be expressed as a sum over expressions (IV.4). Similar to the discussions in Sec. 3, we can represent these expressions as primary graphs. Since in (IV.21) \mathbf{k} is not to be summed over, each of these primary graphs must have one external outgoing line carrying momentum \mathbf{k} and one external incoming line also carrying momentum \mathbf{k} . Thus we can express $M(\mathbf{k})$ as⁹ (proved in Appendix A)

$$M(\mathbf{k}) = z + z^2 \sum [\text{all different primary 1-graphs}] \quad (\text{IV.23})$$

in which each graph contributes a term given by (IV.12).

⁹ It is important to notice that in either (IV.12) or (IV.17) or (IV.26) the factors associated with external lines are not included. Graphically, we adopt the convention that the term corresponding to a graph is given by (IV.12) [or (IV.17) or (IV.26)] except for Figs. 4 and 5. For these two figures the external lines contribute further multiplicative factors $m(\mathbf{k})$ or $M(\mathbf{k})$ as explicitly marked in these graphs.

In a way entirely similar to the reduction of (IV.13) to (IV.18) we can reduce $M(\mathbf{k})$ to a sum over different contracted 1-graphs:

$$M(\mathbf{k}) = m(\mathbf{k}) + [m(\mathbf{k})]^2 \sum [\text{all different contracted 1-graphs}] \quad (\text{IV.24})$$

in which each graph contributes a term given by (IV.17). This sum is illustrated in Fig. 4. The explicit algebraic values of the diagrams are given below⁹:

$$\begin{aligned} M(\mathbf{k}) - m(\mathbf{k}) &= [m(\mathbf{k})]^2 \sum_{\mathbf{k}_1} \langle \mathbf{k}, \mathbf{k}_1 | \Upsilon_2^S | \mathbf{k}, \mathbf{k}_1 \rangle m(\mathbf{k}_1) \\ &+ \frac{1}{2} [m(\mathbf{k})]^2 \sum_{\mathbf{k}_1 \mathbf{k}_2} \langle \mathbf{k}, \mathbf{k}_1, \mathbf{k}_2 | \Upsilon_3^S | \mathbf{k}, \mathbf{k}_1, \mathbf{k}_2 \rangle m(\mathbf{k}_1) m(\mathbf{k}_2) \\ &+ [m(\mathbf{k})]^2 \sum_{\mathbf{k}_1 \mathbf{k}_2} \langle \mathbf{k}, \mathbf{k}_1 | \Upsilon_2^S | \mathbf{k}, \mathbf{k}_1 \rangle \langle \mathbf{k}, \mathbf{k}_2 | \Upsilon_2^S | \mathbf{k}, \mathbf{k}_2 \rangle \\ &\quad \times m(\mathbf{k}_1) m(\mathbf{k}_2) + \dots \quad (\text{IV.25}) \end{aligned}$$

6. IRREDUCIBLE GRAPHS (BOSE STATISTICS)

The above form (IV.24) for $M(\mathbf{k})$ can be further simplified by noticing the property that many of the contracted graphs in Fig. 4 can be generated from a simpler contracted graph by a suitable replacement of the factor $m(\mathbf{q})$ in (IV.17) by $M(\mathbf{q})$. For example, we may take the first contracted graph in the sum for $M(\mathbf{k})$ in Fig. 4 and replace, say, the factors⁹ $m(\mathbf{k}_1)$ and $m(\mathbf{k})$ associated with the internal line and the external outgoing line by $M(\mathbf{k}_1)$ and $M(\mathbf{k})$, respectively. Graphically, we represent $M(\mathbf{k})$ by a thick solid line and illustrate this replacement by changing the appropriate dotted lines into thick solid lines. By using Fig. 4 it is easy to find the totality of contracted graphs represented by this resulting graph.⁹ This is shown in Fig. 5.

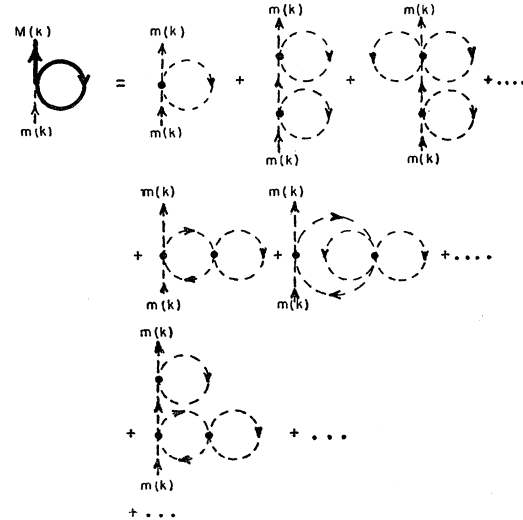


FIG. 5. Graphical example of an irreducible 1-graph as a sum of different contracted 1-graphs. [See reference 9 for the roles of external lines.]

To study such reduction in a systematic way it is necessary to introduce the concept of *reducibility* of a contracted ζ -graph. In the present paper we are only interested in the reducibility for the special cases of $\zeta=0$ and 1.

Definition.—A contracted 0-graph, or a contracted 1-graph, is called *reducible* if by cutting two of its internal lines open the entire graph can be separated into two (or more) disconnected contracted ζ -graphs (ζ can be 1 or 2).

We see, for example, the first two and the fourth contracted 1-graphs in the sum for $[M(\mathbf{k}) - m(\mathbf{k})]$ in Fig. 4 are not reducible while the third and the fifth graphs are reducible.

We now introduce the concept of an *irreducible* graph and its algebraic value.

Definition.—An irreducible ζ -graph is a contracted ζ -graph which is not reducible, with its dotted lines [representing $m(\mathbf{k})$] replaced by thick solid lines [representing $M(\mathbf{k})$]. [Notice that in this terminology an irreducible graph is not just a contracted graph that is not reducible.]

To obtain the value of an irreducible graph we go through the set of procedures (i)–(v) used to obtain (IV.12), except that (iv) is replaced by (iv)''.
(iv)'' Assign a factor $M(\mathbf{k}_i)$ to the i th internal line, where $i=1, 2, \dots, l$.

The term that corresponds to an irreducible graph is given by

$$\sum_{\mathbf{k}_1 \dots \mathbf{k}_l} [\text{product of all factors in (iii), (iv)'', and (v)}]. \quad (\text{IV.26})$$

In terms of irreducible graphs, $M(\mathbf{k})$ can be expressed in a much simpler sum.⁹

$$M(\mathbf{k}) - m(\mathbf{k}) = m(\mathbf{k})M(\mathbf{k})K, \quad (\text{IV.27})$$

where

$$K = \sum [\text{all different irreducible 1-graphs}] \quad (\text{IV.28})$$

in which each graph contributes a term given by (IV.26).

It is important to notice that the role of symmetry numbers is again preserved under this process of reduction.

In explicit form (IV.28) can be written as

$$\begin{aligned} K = & \sum_{\mathbf{k}_1} \langle \mathbf{k}, \mathbf{k}_1 | \Upsilon_2^S | \mathbf{k}, \mathbf{k}_1 \rangle M(\mathbf{k}_1) \\ & + \frac{1}{2} \sum_{\mathbf{k}_1 \mathbf{k}_2} \langle \mathbf{k}, \mathbf{k}_1, \mathbf{k}_2 | \Upsilon_3^S | \mathbf{k}, \mathbf{k}_1, \mathbf{k}_2 \rangle M(\mathbf{k}_1) M(\mathbf{k}_2) \\ & + \frac{1}{2} \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3} \langle \mathbf{k}, \mathbf{k}_1 | \Upsilon_2^S | \mathbf{k}_2 \mathbf{k}_3 \rangle \langle \mathbf{k}_2, \mathbf{k}_3 | \Upsilon_2^S | \mathbf{k}, \mathbf{k}_1 \rangle \\ & \times \prod_1^3 M(\mathbf{k}_i) + \frac{1}{6} \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3} \langle \mathbf{k}, \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3 | \Upsilon_4^S | \mathbf{k}, \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3 \rangle \\ & \times \prod_1^3 M(\mathbf{k}_i) + \dots \quad (\text{IV.29}) \end{aligned}$$

The corresponding irreducible 1-graphs for the sum

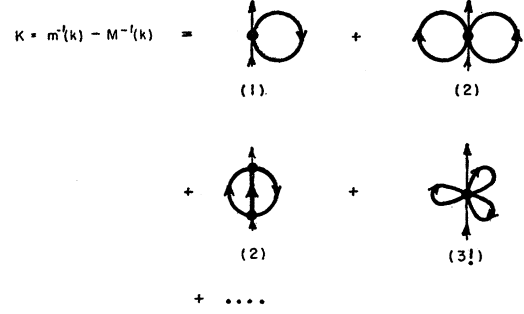


FIG. 6. K [Eq. (IV.28)] as a sum of different irreducible 1-graphs. The corresponding symmetry numbers are listed under these graphs.

(IV.29) are listed in the same order in Fig. 6. The numerical constant in front of each term in the sum (IV.29) is the appropriate factor (symmetry number)⁻¹ of the corresponding irreducible 1-graph in Fig. 6.

(IV.27) is in the form of an integral equation for $M(\mathbf{k})$. By repeated iterations, one can use (IV.27) to express $M(\mathbf{k})$ explicitly in terms of $m(\mathbf{k})$. It is easy to see that the resulting formula is identical with (IV.24).

It may be emphasized that while formally the sum over contracted graphs, (IV.24), is equivalent to the sum over irreducible graphs, (IV.27), this regrouping of infinitely many contracted graphs into fewer irreducible graphs is actually important in avoiding unnecessary infinities as z approaches one.

To understand this, let us consider any reducible graph in the sum (IV.24). In such a graph, because of conservation of momentum some of the momenta (associated with different lines) must be identical.¹⁰ In cases where these identical momenta are associated with internal lines, say, $1 \dots n$, such a reducible graph would contribute to the sum (IV.24) a term of the form

$$\int [m(\mathbf{q})]^n d^3q G(\mathbf{q}), \quad (\text{IV.30})$$

where $G(\mathbf{q})$ represents the factors from the other elements of the graph such as vertices, etc. At $z=1$, $m(\mathbf{q})$ has a singularity at $\mathbf{q}=0$. Thus (IV.30) behaves like

$$G(\mathbf{q}=0)[1-z]^{1-n} \quad (\text{IV.31})$$

as $z \rightarrow 1-$. Consequently, to obtain the form of $M(\mathbf{k})$ as z nears 1 it is necessary in (IV.24) to sum over all such singular terms (IV.31), especially for large values of n . The result of these infinite sums over various reducible graphs is precisely the final form (IV.27).

Thus, the reduction of contracted graphs to irre-

¹⁰ For example, in the fifth graph in the sum in Fig. 4, the two momenta in the middle loop must be identical. In general, by definition, a reducible graph can be separated into two parts A and B connected by not more than two lines. (Both A and B must each contain some vertices.) In the case that A and B are connected by two lines the momenta associated with these two lines must be identical. Otherwise, [e.g., in the third graph in Fig. 3] the momentum associated with the single line which connects A and B must be the same as that of the external line.

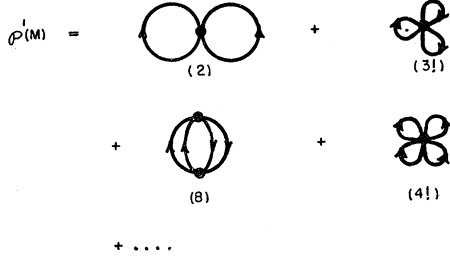


FIG. 7. $\phi^{(M)}$ [Eq. (IV.34)] as a sum over different irreducible 0-graphs. The corresponding symmetry numbers are listed under these graphs.

ducible graphs represents not only a mathematical simplification but also a physical necessity as $z \rightarrow 1$.

In terms of $M(\mathbf{k})$ we can also express the pressure p of any Bose system in a finite volume Ω as a sum over different irreducible 0-graphs (proved in Appendix C),

$$(\kappa T)^{-1} \Omega p = \mathcal{O}(z, M), \quad (\text{IV.32})$$

where

$$\begin{aligned} \mathcal{O}(z, M) \equiv & \sum_{\mathbf{k}} \ln [z^{-1} M(\mathbf{k})] \\ & - \sum_{\mathbf{k}} [m(\mathbf{k})]^{-1} [M(\mathbf{k}) - m(\mathbf{k})] \\ & + \sum [\text{all different irreducible 0-graphs}], \end{aligned} \quad (\text{IV.33})$$

in which each graph contributes a term given by (IV.26). More explicitly, if we define ϕ' to be the sum over all different irreducible 0-graphs, then

$$\begin{aligned} \phi'(z, M) &= \frac{1}{2} \sum_{\mathbf{k}_1, \mathbf{k}_2} \langle \mathbf{k}_1, \mathbf{k}_2 | \Upsilon_2^S | \mathbf{k}_1, \mathbf{k}_2 \rangle \prod_{i=1}^2 M(\mathbf{k}_i) \\ &+ \frac{1}{6} \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} \langle \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3 | \Upsilon_3^S | \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3 \rangle \prod_{i=1}^3 M(\mathbf{k}_i) \\ &+ \frac{1}{8} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_4} [\langle \mathbf{k}_1, \mathbf{k}_2 | \Upsilon_2^S | \mathbf{k}_3, \mathbf{k}_4 \rangle] \\ &\times [\langle \mathbf{k}_3, \mathbf{k}_4 | \Upsilon_2^S | \mathbf{k}_1, \mathbf{k}_2 \rangle] \prod_{i=1}^4 M(\mathbf{k}_i) \\ &+ \frac{1}{4!} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_4} \langle \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4 | \Upsilon_4^S | \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4 \rangle \\ &\times \prod_{i=1}^4 M(\mathbf{k}_i) + \dots \end{aligned} \quad (\text{IV.34})$$

In (IV.34) the first four terms correspond to, respectively, the four irreducible 0-graphs in Fig. 7.

7. VARIATIONAL PRINCIPLES

In this section we shall discuss some general variational properties.

1. In (IV.33) we regard \mathcal{O} as an explicit functional of z and $M(\mathbf{k})$. It is shown in Appendix C that if we set the variation of $\mathcal{O}(z, M)$ with respect to M to be zero,

$$\left[\frac{\delta}{\delta M(\mathbf{k})} \mathcal{O}(z, M) \right]_z = 0, \quad (\text{IV.35})$$

then the integral equation (IV.27) for M follows automatically.

Furthermore, if we denote the second functional derivatives of \mathcal{O} by a matrix $R_{\mathbf{k}\mathbf{k}'}$,

$$R_{\mathbf{k}\mathbf{k}'} \equiv \left[\frac{\delta^2 \mathcal{O}}{\delta M(\mathbf{k}) \delta M(\mathbf{k}')} \right]_z, \quad (\text{IV.36})$$

then at the point that (IV.35) is true, the inverse R^{-1} of this matrix is given by [proved in Appendix D]

$$\begin{aligned} (R^{-1})_{\mathbf{k}\mathbf{k}'} &= -z M(\mathbf{k}) \delta_{\mathbf{k}\mathbf{k}'} \\ &\quad - z^2 \langle (n_{\mathbf{k}} - \langle n_{\mathbf{k}} \rangle) (n_{\mathbf{k}'} - \langle n_{\mathbf{k}'} \rangle) \rangle, \end{aligned} \quad (\text{IV.37})$$

where $\langle \rangle$ means statistical average over the grand canonical ensemble and $\delta_{\mathbf{k}\mathbf{k}'}$ is the Kronecker δ -symbol. Thus, $R_{\mathbf{k}\mathbf{k}'}$ is a negative matrix [i.e., its eigenvalues are always negative]. Combining (IV.35) and (IV.37), we find that if we regard $\mathcal{O}(z, M)$ as a functional of an arbitrary function $M(\mathbf{k})$ then the pressure of the system is given by¹¹

$$\Omega p (\kappa T)^{-1} = \text{maximum} [\mathcal{O}(z, M)] \quad (\text{IV.38})$$

at constant z .

It is of interest to notice that (IV.38) holds for a finite, as well as for an infinite, volume.

Upon taking the derivative of \mathcal{O} with respect to $\ln z$ we have, by using (IV.22),

$$\left[\frac{\partial}{\partial \ln z} \mathcal{O}(z, M) \right]_M = \Omega \rho, \quad (\text{IV.39})$$

where ρ is the particle density of the system.

2. From (IV.32), the free energy F of the system can be readily evaluated if $M(\mathbf{k})$ is known. It is useful to express F as an explicit functional of ρ and $M(\mathbf{k})$,

$$(\kappa T)^{-1} F = \mathfrak{F}(\rho, M). \quad (\text{IV.40})$$

The functional $\mathfrak{F}(\rho, M)$ is given by the Legendre transformation

$$\mathfrak{F}(\rho, M) \equiv \Omega \rho \ln z - \mathcal{O}(z, M), \quad (\text{IV.41})$$

in which we use (IV.39) and regard

$$z = z(\rho, M). \quad (\text{IV.42})$$

The functional derivatives of \mathfrak{F} with respect to M at constant ρ are related to the derivatives of \mathcal{O} by

$$\left[\frac{\delta \mathfrak{F}}{\delta M(\mathbf{k})} \right]_{\rho} = - \left[\frac{\delta \mathcal{O}}{\delta M(\mathbf{k})} \right]_z, \quad (\text{IV.43})$$

and

$$\left[\frac{\delta^2 \mathfrak{F}}{\delta M(\mathbf{k}) \delta M(\mathbf{k}')} \right]_{\rho} = - \left[\frac{\delta^2 \mathcal{O}}{\delta M(\mathbf{k}) \delta M(\mathbf{k}')} \right]_z. \quad (\text{IV.44})$$

Consequently, if we regard \mathfrak{F} as a functional of an arbitrary function $M(\mathbf{k})$, then the Helmholtz free

¹¹ It will be further shown in Appendix D that under certain general conditions this maximum is also an absolute maximum

energy is given by

$$(\kappa T)^{-1}F = \text{minimum} [\mathcal{F}(\rho, M)] \quad (\text{IV.45})$$

at constant ρ .

Although these functions $\mathcal{O}(z, M)$ and $\mathcal{F}(\rho, M)$ are expressed in terms of infinite sums of irreducible 0-graphs, it is important to notice that especially for a dilute Bose system at low temperature the various irreducible 0-graphs contribute quite differently to these sums.

For definiteness, let us consider a dilute Bose system of hard spheres of radius a in its *gaseous state*. For such a system it is possible to estimate directly the magnitudes of different terms in the sum (IV.34). Let us consider a typical irreducible 0-graph with m_α α -vertices and l internal lines,

$$\sum_{\alpha=2}^{\infty} m_\alpha \alpha = l.$$

Such a graph would contribute a term of the form

$$\sum_{\mathbf{k}_1 \dots \mathbf{k}_l} [\prod \Upsilon_\alpha^S] [\prod M(\mathbf{k}_i)] \quad (\text{IV.46})$$

to the sum (IV.34). Since the system is in the gaseous state, and since $M(\mathbf{k})$ is related to the physical quantities $\langle n_k \rangle$ and the fugacity z by (IV.20), we find

$$M(\mathbf{k}) = \text{finite} \propto \rho \lambda^3, \quad (\text{IV.47})$$

where $\lambda^2 = (4\pi\beta)$.

We recall that for small a [see Appendix E and paper III¹²],

$$\langle 1' 2' \dots \alpha' | \Upsilon_\alpha^S | 1 2 \dots \alpha \rangle \propto (a\lambda^2/\Omega)^{\alpha-1} \quad (\text{IV.48})$$

for small values of \mathbf{k}_i and decreases exponentially like $\exp(-\beta \mathbf{k}_i^2)$ for large \mathbf{k}_i . Thus in each summation over \mathbf{k}_i only regions $|\mathbf{k}_i| \lesssim \lambda^{-1}$ are of importance. Because of momentum conservation there are $(l - \sum m_\alpha + 1)$ independent momenta to be summed over. Combining all these factors, it is easy to see that (IV.46) is of the magnitude

$$\Omega \lambda^{-3} (a/\lambda)^{l-n} (\rho \lambda^3)^l, \quad (\text{IV.49})$$

where n is the total number of vertices in the graph:

$$n = \sum_{\alpha=2}^{\infty} m_\alpha. \quad (\text{IV.50})$$

8. APPROXIMATION METHODS AND APPLICATIONS

We shall show that for a Bose system of hard spheres at given ρ and T in the *gaseous phase*, all the thermodynamical functions can be evaluated systematically provided a is small [i.e., $(a\rho\lambda^3) \ll 1$ and $(a/\lambda) \ll 1$].

As $\Omega \rightarrow \infty$, we can replace all summation over momentum space by continuous integration. Thus

¹² T. D. Lee and C. N. Yang, Phys. Rev. **117**, 12 (1960), Sec. 3.

(IV.22), (IV.41), and (IV.34) become, respectively,

$$\rho = (8\pi^3)^{-1} \int [z^{-1} M(\mathbf{k}) - 1] d^3 k, \quad (\text{IV.51})$$

$$\begin{aligned} \Omega^{-1} \mathcal{F}(\rho, M) &= \rho \ln z - (8\pi^3)^{-1} \int \ln [z^{-1} M(\mathbf{k})] d^3 k \\ &\quad + (8\pi^3)^{-1} \int [m(\mathbf{k})]^{-1} \\ &\quad \times [M(\mathbf{k}) - m(\mathbf{k})] d^3 k - \Omega^{-1} \mathcal{O}', \end{aligned} \quad (\text{IV.52})$$

and

$$\begin{aligned} (8\pi^3) \Omega^{-1} \mathcal{O}'(M) &= \frac{1}{2} \int \langle \mathbf{k}_1, \mathbf{k}_2 | v_2^S | \mathbf{k}_1, \mathbf{k}_2 \rangle \prod_{i=1}^2 M(\mathbf{k}_i) d^3 k_i \\ &\quad + \frac{1}{8} \int [\langle \mathbf{k}_1, \mathbf{k}_2 | v_2^S | \mathbf{k}_3, \mathbf{k}_4 \rangle]^2 \delta^3(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3 - \mathbf{k}_4) \\ &\quad \times \prod_{i=1}^4 M(\mathbf{k}_i) d^3 k_i + \frac{1}{6} \int \langle \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3 | v_3^S | \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3 \rangle \\ &\quad \times \prod_{i=1}^3 M(\mathbf{k}_i) d^3 k_i + \dots, \end{aligned} \quad (\text{IV.53})$$

where v_i^S are related to the Boltzmann u_i functions [defined in Eq. (I.54) of paper I] by

$$\begin{aligned} \langle \mathbf{k}_1', \dots, \mathbf{k}_l' | v_l^S | \mathbf{k}_1, \dots, \mathbf{k}_l \rangle \\ = \sum_{P'} P' \langle \mathbf{k}_1', \dots, \mathbf{k}_l' | u_l | \mathbf{k}_1, \dots, \mathbf{k}_l \rangle, \end{aligned} \quad (\text{IV.54})$$

and are independent of the volume. In (IV.54) the sum extends over all permutations of $\mathbf{k}_1', \dots, \mathbf{k}_l'$. In proving (IV.53) the detailed relationship between Υ_l^S and v_l^S discussed in Appendix E is used.

(IV.49) gives a direct classification of the magnitudes of each term in the infinite sum (IV.53) as powers of a . To calculate, for example, the free energy F accurate to a certain power in a , we can neglect all those terms in (IV.53) which give only higher order contributions. The corresponding approximate integral equation for M can be generated by the variational principle

$$[\delta \mathcal{F} / \delta M(\mathbf{k})]_p = 0, \quad (\text{IV.55})$$

which automatically insures the consistency between the two approximate formulas for M and for F .

In the following, we shall solve for z , $M(\mathbf{k})$ and F explicitly as functions of ρ and in powers of a . The n th order approximate solutions [accurate to $O(a^n)$] will all be denoted by subscripts n .

Zeroth Approximation

In the zeroth approximation we do not include any irreducible 0-graph.

$$\mathcal{O}'_0 = 0. \quad (\text{IV.56})$$

The zeroth order solution for $M(\mathbf{k})$ is

$$M_0(\mathbf{k}) = z_0 [1 - z_0 \exp(-\beta \mathbf{k}^2)]^{-1} \quad (\text{IV.57})$$

where z_0 , as a function of ρ and T , is given by

$$\rho = \lambda^{-3} g_3(z_0), \quad g_l(z) = \sum_{n=1}^{\infty} z^n n^{-l}. \quad (\text{IV.58})$$

Correspondingly, the zeroth order free energy is

$$(\Omega \kappa T)^{-1} F_0 = \rho \ln z_0 - \lambda^{-3} g_{\frac{5}{2}}(z_0). \quad (\text{IV.59})$$

The zeroth approximation is identical with that of a free Bose gas.

First Approximation

There is only one irreducible 0-graph which contributes to the order of a . Hence,

$$(8\pi^3) \Omega^{-1} \mathcal{P}_1' = \frac{1}{2} \int \langle \mathbf{k}_1 \mathbf{k}_2 | v_2^S | \mathbf{k}_1 \mathbf{k}_2 \rangle \times M(\mathbf{k}_1) M(\mathbf{k}_2) d^3 k_1 d^3 k_2. \quad (\text{IV.60})$$

Because of the variational character of the free energy, we can substitute directly the zeroth order solution z_0 , $M_0(\mathbf{k})$ into (IV.52) and obtain the first order expression for F . Substituting (IV.57), (IV.58) and the explicit form of v_2^S [see Eq. (I.67) of I]

$$\langle \mathbf{k}_1 \mathbf{k}_2 | v_2^S | \mathbf{k}_1 \mathbf{k}_2 \rangle = (2\pi^3)^{-1} a \lambda^2 \times \exp[-\beta(\mathbf{k}_1^2 + \mathbf{k}_2^2)] + O(a^2) \quad (\text{IV.61})$$

into (IV.60), we obtain [neglecting $O(a^2)$]

$$\Omega^{-1} \mathcal{P}_1' = -2a \lambda^2 \rho^2. \quad (\text{IV.62})$$

Correspondingly, we find the first order expression for F to be

$$(\kappa T \Omega)^{-1} F_1 = \rho \ln z_0 - \lambda^{-3} g_{\frac{5}{2}}(z_0) + 2a \lambda^2 \rho^2, \quad (\text{IV.63})$$

where z_0 is given by (IV.58). Using (IV.63) we can obtain the first order expression for p as

$$p_1 = \lambda^{-3} (\kappa T) g_{\frac{5}{2}}(z_0) + 8\pi a \rho^2. \quad (\text{IV.64})$$

Expressions (IV.63) and (IV.64) are identical with the results obtained by the pseudopotential method.¹³

To obtain the first order solution M_1 and z_1 , we have to use (IV.60) and apply the variational principle (IV.55). The resulting equation is

$$-M_1^{-1}(\mathbf{k}) + z_1^{-1} - \exp(-\beta \mathbf{k}^2) + (2\pi^3)^{-1} a \lambda^2 \times \exp(-\beta \mathbf{k}^2) \int M(\mathbf{q}) \exp(-\beta \mathbf{q}^2) d^3 q = 0, \quad (\text{IV.65})$$

which can be readily solved. The first order solutions M_1 and z_1 are given by

$$M_1(\mathbf{k}) = z_1 [1 - \xi \exp(-\beta \mathbf{k}^2)]^{-1}, \quad (\text{IV.66})$$

$$\rho = \lambda^{-3} g_{\frac{3}{2}}(\xi), \quad (\text{IV.67})$$

¹³ T. D. Lee and C. N. Yang, Phys. Rev. **112**, 1419 (1958).

where

$$\xi = z_1 \left[1 - (2\pi^3)^{-1} a \lambda^2 \int M_1(\mathbf{q}) \exp(-\beta \mathbf{q}^2) d^3 q \right]. \quad (\text{IV.68})$$

Second Approximation

To calculate F to $O(a^2)$ we have to include in \mathcal{P}_2' the first three terms in (IV.53). Because of the minimum property of \mathcal{F} we can substitute the first order solutions $z_1(\rho, T)$ and $M_1(\rho, T, \mathbf{k})$ into \mathcal{P}_2' and directly obtain the second order expression for F .

9. SINGULARITY OF $M(\mathbf{k})$

From these approximate solutions we expect that there exists a critical value z_c . At $z < z_c$, $M(\mathbf{k})$ is finite for all \mathbf{k} values; but, at $z = z_c$, $M(\mathbf{k})$ becomes infinite at $\mathbf{k} = 0$. In general we may write (IV.27) as

$$-M^{-1}(\mathbf{k}) + m^{-1}(\mathbf{k}) = K(\mathbf{k}). \quad (\text{IV.69})$$

Thus, the condition for z_c is

$$z_c^{-1} = 1 + K(\mathbf{k} = 0). \quad (\text{IV.70})$$

By using the approximate solutions we can evaluate z_c as a power series in a . Substituting (IV.66) in (IV.70) we have

$$z_c = 1 + 4(2.612)(a/\lambda) + \dots \quad (\text{IV.71})$$

Correspondingly, the density and the pressure at $z = z_c$ are given by

$$\lambda^3 \rho_c = (2.612) + O(a/\lambda),$$

and

$$\lambda^3 (\kappa T)^{-1} p_c = (1.342) + 2(2.612)^2 (a/\lambda) + \dots \quad (\text{IV.72})$$

As will be shown in detail in paper V, such singular behavior of $M(\mathbf{k})$ at $\mathbf{k} = 0$ is a general characteristic of a Bose-Einstein phase transition. Physically, it means that in the condensed phase

$$M(\mathbf{k} = 0) = x \rho \Omega, \quad (\text{IV.73})$$

where x is a finite number between 0 and 1. Consequently, $M(\mathbf{k} = 0)$ becomes infinite as $\Omega \rightarrow \infty$.

It is of course true that even though $M(\mathbf{k} = 0)$ may be proportional to Ω , our present formalism still is formally valid. However, if $x \neq 0$, then unless a further re-grouping of the series is performed, our basic equations in terms of irreducible graphs cannot be used. Indeed, e.g., the sum (IV.34) is a series consisting of infinite members of increasingly divergent terms. To show this, let us consider a typical irreducible 0-graph (IV.46). By using (IV.73) and (IV.48), we find that if $x \neq 0$, (IV.46) is proportional to

$$x^l \Omega^n \quad (\text{IV.74})$$

plus terms proportional to lower powers in Ω . The maximum power n is equal to the total number of

vertices in the graph:

$$n = \sum_{\alpha=2}^{\infty} m_{\alpha}.$$

Consequently, if $x \neq 0$, the higher order terms in the sums (IV.28) and (IV.34) become more and more divergent as $\Omega \rightarrow \infty$.

In paper V, we shall give a new formalism which reduces to the present one in the gaseous phase ($x=0$). But unlike the present one it can be applied also in the condensed phase and does not contain the above-mentioned divergence difficulties.

10. FERMI STATISTICS

In this section we consider a system of Fermi particles with spin J in a finite volume Ω . The grand partition function \mathcal{Q}_{Ω}^A is given by

$$\ln \mathcal{Q}_{\Omega}^A = \sum_{l=1}^{\infty} (l!)^{-1} z^l \sum_{q_1 \cdots q_l} \langle q_1 \cdots q_l | U_l^A | q_1 \cdots q_l \rangle, \quad (\text{IV.75})$$

where q_i represents both the momentum and the spin coordinates of the i th particle ($i=1, 2, \dots, l$). Starting from rule *B* of paper I, we can also formulate \mathcal{Q}_{Ω}^A in terms of the average occupation number by procedures similar to those used in the previous sections.

Let $\langle n_q \rangle$ be the statistical (averaged over a grand canonical ensemble) average number of particles with a definite momentum and a definite spin component. Both of these coordinates are represented by q . The corresponding function $M^A(q)$ is defined by

$$M^A(q) \equiv z[1 - \langle n_q \rangle]. \quad (\text{IV.76})$$

The particle density ρ is related to M^A by

$$\Omega \rho = \sum_q [1 - z^{-1} M^A(q)]. \quad (\text{IV.77})$$

Similarly to (IV.21), M^A can also be expressed in terms of U_l^A (proved in Appendix B),

$$M^A(q) = z - \sum_{l=1}^{\infty} [(l-1)!]^{-1} z^{l+1} \times \sum_{q_1 \cdots q_{l-1}} \langle q_1 \cdots q_{l-1}, q | U_l^A | q_1 \cdots q_{l-1}, q \rangle. \quad (\text{IV.78})$$

Next we define a primary ζ -graph, a contracted ζ -graph, and an irreducible ζ -graph ($\zeta=0, 1, 2, \dots$) in exactly the same way as in the Bose case. To each of these graphs we assign a term, slightly different from its counterpart in the Bose case, determined by the following procedures for $\zeta=0$ or 1:

(*iA*) Associate with each internal line a different integer i ($i=1, 2, \dots, l$) and its corresponding q_i .

(*iiA*) Associate each of the external lines with some pre-given momenta and spin values.

(*iiiA*) Assign a factor

$$\langle q_{B_1} \cdots q_{B_{\alpha}} | \Upsilon_{\alpha}^A | q_{A_1} \cdots q_{A_{\alpha}} \rangle$$

to each α -vertex where $q_{A_1} \cdots q_{A_{\alpha}}$ and $q_{B_1} \cdots q_{B_{\alpha}}$ are the momenta and spins associated with its (internal or external) incoming and outgoing lines, respectively. The definition of Υ_{α}^A is given by (I.31).

(*ivA*) To each i th *internal* lines, we assign a factor z in the case of a primary graph, a factor

$$m^A(q_i) \equiv z[1 + z \exp(-\beta \mathbf{k}_i^2)]^{-1} \quad (\text{IV.79})$$

in the case of a contracted graph, and a factor $M^A(q_i)$ in the case of an irreducible graph. In (IV.79), \mathbf{k}_i is the momentum represented by q_i .

(*vA*) Assign a factor

$$(\text{symmetry number})^{-1},$$

to the entire graph. The definition of the symmetry number is identical with that in the Bose case.

(*viA*) Assign a factor \mathcal{C} to the entire graph. Here \mathcal{C} is $+1$ (or -1) if the permutation

$$q_{A_1} \rightarrow q_{B^1}, \quad q_{A_2} \rightarrow q_{B^2}, \quad \dots, \quad q_{A_{\alpha}} \rightarrow q_{B^{\alpha}}, \quad \dots$$

from all the initial coordinates into all the final coordinates of all the vertex functions Υ_{α}^A taken together is even (or odd).

The term that corresponds to each graph is given by

$$\sum_{q_1 \cdots q_l} [\text{product of all factors in (iiiA), (ivA), (vA) and (viA)}]. \quad (\text{IV.80})$$

In terms of these graphs, we can write in complete analogy with (IV.13), (IV.18), and (IV.33)

$$(\kappa T)^{-1} \Omega p = \sum [\text{all different primary 0-graphs}], \quad (\text{IV.81})$$

$$= - \sum_q \ln [z^{-1} m^A(q)]$$

$$+ \sum [\text{all different contracted 0-graphs}], \quad (\text{IV.82})$$

$$= - \sum_q \ln [z^{-1} M^A(q)]$$

$$+ \sum [m^A(q)]^{-1} [M^A(q) - m^A(q)]$$

$$+ \sum [\text{all different irreducible 0-graphs}]. \quad (\text{IV.83})$$

Similarly,

$$M^A(q) = z - z^2 \sum [\text{all different primary 1-graphs}], \quad (\text{IV.84})$$

$$= m^A(q) - [m^A(q)]^2 \sum [\text{all different contracted 1-graphs}], \quad (\text{IV.85})$$

$$= m^A(q) - [m^A(q) M^A(q)] \sum [\text{all different irreducible 1-graphs}]. \quad (\text{IV.86})$$

In the above equations (IV.81)–(IV.86) each graph contributes a term given by (IV.80). [Notice the difference in factors (*ivA*) for primary, contracted and irreducible graphs.] The first few terms of (IV.82) have been derived also in paper II.

In a similar manner to that for the Bose system, a variational principle can be obtained for the Fermi system.

APPENDIX A

We first discuss an elementary property of the symmetry number.

Let us assign a different integer i ($i=1, 2, \dots, l$) to every internal line of a ζ -graph. The resulting graph is called a *numbered ζ -graph generated* from the original graph.¹⁴ Two numbered ζ -graphs are different only if they have different topological structures, including the positions of these numbers.

Let D be the total number of different numbered ζ -graphs which can be generated from the same ζ -graph. From the definition of symmetry number given by (IV.11), it is easy to see that

$$D = (l!)s^{-1}, \quad (\text{IV.87})$$

where s and l are, respectively, the symmetry number and the number of internal lines in the original ζ -graph.

To prove (IV.13) and (IV.23), we notice that different terms in (IV.4) [e.g. (Ai) and (Aii) given by (IV.8) and (IV.9)] can give identical results after summing over all their *internal* momenta. Graphically these terms correspond to the same primary ζ -graph but different numbered primary ζ -graphs [e.g., $(Ai)'$ and $(Aii)'$ in Fig. 1]. Thus, the total number of such terms is identical with the total number, D of the corresponding different numbered ζ -graphs. In both (IV.1) and (IV.21) we have to sum over such terms, sum over their internal momenta $\mathbf{k}_1 \dots \mathbf{k}_l$, and then divide by $(l!)$. Consequently, we obtain a factor

$$(l!)^{-1}D,$$

which is, by (IV.87), $(\text{symmetry number})^{-1}$. By using (IV.12), it then follows that (IV.13) and (IV.23) correctly express the sums (IV.1) and (IV.21), respectively.

APPENDIX B

To prove (IV.19) and (IV.78), we recall that in the sum

$$\mathcal{Q}_\Omega^\alpha = \sum_{N=0}^{\infty} (N!)^{-1} z^N \sum_{1 \dots N} \langle 1, \dots, N | W_N^\alpha | 1, \dots, N \rangle, \quad (\text{IV.88})$$

[$\alpha = s, A$ depending on the statistics],

each term represents a relative probability. Thus, the statistical value $\langle n_q \rangle$ of particles with momentum (and spin coordinate) q averaged over a grand canonical ensemble is

$$\begin{aligned} & (\mathcal{Q}_\Omega^\alpha)^{-1} \sum_{N=0}^{\infty} [(N-1)!]^{-1} z^N \\ & \times \sum_{1, \dots, N-1} \langle 1, 2, \dots, N-1, q | W_N^\alpha | 1, 2, \dots, N-1, q \rangle. \end{aligned} \quad (\text{IV.89})$$

¹⁴ For simplicity, a ζ -graph (or a numbered ζ -graph) refers to a primary or a contracted or an irreducible ζ -graph (or the corresponding numbered ζ -graph).

In (IV.89) we have utilized the property that $\langle 1, \dots, N | W_N^\alpha | 1, \dots, N \rangle$ is a symmetric function with respect to the N particles. We now use the definitions of U_l^α [e.g., (I.12) of paper I] and observe that each W_N^α can be written as a sum over products of the form

$$\langle q, a_1, \dots, a_{n-1} | U_n^\alpha | q, a_1, \dots, a_{n-1} \rangle \times \langle b_1, \dots, b_l | U_l^\alpha | b_1, \dots, b_l \rangle \dots \quad (\text{IV.90})$$

In general, (IV.90) is a product of one U_n^α which contains q as one of its variables, and $m_1 U_1^\alpha$ functions, $m_2 U_2^\alpha$ functions, etc., which contain other particles as variables. In $\langle 1, \dots, N-1, q | W_N^\alpha | 1, \dots, N-1, q \rangle$, there are altogether

$$\frac{(N-1)!}{(n-1)! \prod_i [(l!)^{m_i} (m_i)]} \quad (\text{IV.91})$$

such terms where

$$N = n + \sum_{l=1}^{\infty} l m_l. \quad (\text{IV.92})$$

Each of such terms contributes a term

$$\left[\sum_{1, \dots, n-1} \langle q, 1, \dots, n-1 | U_n^\alpha | q, 1, \dots, n-1 \rangle \prod_i [l! \Omega b_l(\Omega)]^{m_i} \right] \quad (\text{IV.93})$$

to the sum

$$\sum_{1, \dots, N-1} \langle q, 1, \dots, N-1 | W_N^\alpha | q, 1, \dots, N-1 \rangle.$$

Substituting these factors into (IV.89), we find

$$\begin{aligned} \langle n_q \rangle &= \sum_{n=1}^{\infty} [(n-1)!]^{-1} z^n \\ &\times \sum_{1, \dots, n-1} \langle q, 1, \dots, n-1 | U_n^\alpha | q, 1, \dots, n-1 \rangle. \end{aligned} \quad (\text{IV.94})$$

If we define the corresponding $M^\alpha(q)$ to be

$$M^\alpha(q) \equiv z[1 \pm \langle n_q \rangle], \quad (\text{IV.95})$$

with $+$ sign for $\alpha = S$, $-$ sign for $\alpha = A$ (in the text, the superscript $\alpha = S$ is omitted), then $M^S(q)$ and $M^A(q)$ are given, respectively, by (IV.21) and (IV.78).

It is of interest to notice that in terms of second quantized field operators, $M^\alpha(q)$ can be written as

$$\begin{aligned} z^{-1} M^\alpha(q) &= (\mathcal{Q}_\Omega^\alpha)^{-1} \text{trace} [a^\dagger(q) \\ &\times \exp(-\beta \mathcal{H}) z^{\mathfrak{N}} a(q)], \end{aligned} \quad (\text{IV.96})$$

where $a(q)$, $a^\dagger(q)$ are the appropriate annihilation and creation operators and \mathcal{H} , \mathfrak{N} are, respectively, the second quantized operators for the Hamiltonian and the total number of particles.

APPENDIX C

Equation (IV.32) asserts that

$$\ln \mathcal{Q}_\Omega^S = \mathcal{P}(z, M), \quad (\text{IV.97})$$

for all values of $z \geq 0$. In this formula the left-hand side is a function of z defined in (IV.1), and the right-hand

side is defined as a functional of z , M through (IV.33) while M is in turn defined by (IV.21), or equivalently (IV.27). To prove (IV.97), one notices that as $z \rightarrow 0$, by their definitions,

$$\mathcal{Q}_\Omega^S \rightarrow 1, \quad M(\mathbf{k}) \rightarrow z, \quad m(\mathbf{k}) \rightarrow z.$$

Thus, (IV.97) is correct at $z=0$. We now proceed to prove that the derivatives of both sides with respect to $\ln z$ are the same for all $z \geq 0$. The derivative with respect to $\ln z$ of the left-hand side is, by (IV.22)

$$\sum_{\mathbf{k}} [z^{-1} M(\mathbf{k}) - 1]. \quad (\text{IV.98})$$

That of the right-hand side, by the rules of implicit differentiation is:

$$\left(\frac{\partial \mathcal{P}}{\partial \ln z} \right)_M + \sum_{\mathbf{k}} \left(\frac{\delta \mathcal{P}}{\delta M(\mathbf{k})} \right)_z \frac{dM(\mathbf{k})}{dz}. \quad (\text{IV.99})$$

Now, in (IV.33) the irreducible 0-graphs are dependent on z only implicitly through M . Hence, using the explicit form of $M(\mathbf{k})$, one obtains

$$\left(\frac{\partial \mathcal{P}}{\partial \ln z} \right)_M = -1 + \sum_{\mathbf{k}} z^{-1} M(\mathbf{k}) = (\text{IV.98}).$$

Thus to prove (IV.97), it is only necessary to prove

$$\left(\frac{\delta \mathcal{P}}{\delta M(\mathbf{k})} \right)_z = 0 \quad (\text{IV.100})$$

for the values of M satisfying (IV.27), i.e., satisfying

$$M^{-1}(\mathbf{k}) = m^{-1}(\mathbf{k}) - K(\mathbf{k}, M). \quad (\text{IV.101})$$

Using (IV.101), we can write (IV.100) in the form

$$\left. \frac{\delta}{\delta M(\mathbf{k})} \right|_z \sum [\text{all different irreducible 0-graphs}] = K(\mathbf{k}, M),$$

or, by (IV. 28), in the form

$$\begin{aligned} \frac{\delta}{\delta M(\mathbf{k})} \sum [\text{all different irreducible 0-graphs}], \\ = \sum [\text{all different irreducible 1-graphs}]. \end{aligned} \quad (\text{IV.102})$$

Now (IV.102) is an identity. It is correct even if (IV.101) is not satisfied, and all $M(\mathbf{k})$ are independently and freely variable.

To prove this statement, we take as an illustration the first irreducible 0-graph in column A, Fig. 2. It is equal to

$$\frac{1}{2} \sum_{\mathbf{k}_1 \mathbf{k}_2} \langle \mathbf{k}_1, \mathbf{k}_2 | \Upsilon_2^S | \mathbf{k}_1, \mathbf{k}_2 \rangle M(\mathbf{k}_1) M(\mathbf{k}_2).$$

Differentiation with respect to $M(\mathbf{k})$ yields

$$2 \left(\frac{1}{2} \right) \sum_{\mathbf{k}_2} \langle \mathbf{k}, \mathbf{k}_2 | \Upsilon_2^S | \mathbf{k}, \mathbf{k}_2 \rangle M(\mathbf{k}_2),$$

which is the first irreducible 1-graph in column B, Fig. 2. The other graphs in Fig. 2 give similar results.

For a general irreducible 0-graph we first define a relationship, to be called *correspondence*, between the 0-graphs and the 1-graphs.¹⁴ If we take any 0-graph and cut any one of its lines open, the resulting graph is a 1-graph. Conversely, by connecting together the two external lines of a 1-graph we obtain a 0-graph. Furthermore, if the 0-graph is an irreducible graph then *its corresponding 1-graphs are all irreducible*.

By cutting open one of the l lines of an irreducible 0-graphs one obtains a corresponding 1-graph. Varying the line that is cut leads to l corresponding 1-graphs. Among these, a particular 1-graph may occur, say, n times. Let S_0 and S_1 be, respectively, the symmetry numbers of the irreducible 0-graph and this particular 1-graph. From the definition of symmetry number it is straightforward to show that

$$S_0 = n S_1. \quad (\text{IV.103})$$

Equation (IV.103) is illustrated in Fig. 2.

To prove (IV.102), one notices that in taking the functional derivative $\delta/\delta M(\mathbf{k})$ of any irreducible 0-graph with l lines, one generates l terms each of which is equal to $S_0^{-1} S_1$ times a corresponding 1-graph, which is obtained by cutting open one of the l lines. Equation (IV.102), then, follows immediately by using (IV.103).

We remark that (IV.100) proves also the stationary property of \mathcal{P} with respect to variations $\delta M(\mathbf{k})$, as stated in (IV.35).

APPENDIX D

The functional $\mathcal{P}(z, M)$ will be written in this Appendix in the form

$$\mathcal{P}(z, M) = \sum_{\mathbf{k}} \ln [z^{-1} M(\mathbf{k})] - \sum_{\mathbf{k}} \{ [z^{-1} - \exp(-\beta \mathbf{k}^2)] M(\mathbf{k}) - 1 \} + \mathcal{P}' \quad (\text{IV.104})$$

where $\mathcal{P}'(M) = \sum$ all different irreducible 0-graphs.

We recall that from (IV.102) one obtains

$$\frac{\delta \mathcal{P}'}{\delta M(\mathbf{k})} = K(\mathbf{k}, M).$$

The functional derivative of \mathcal{P} at fixed z vanishes for M satisfying the equilibrium distribution, as shown by (IV.35). To obtain the second (functional) derivative of \mathcal{P} we shall regard z and T as fixed. Furthermore in this Appendix we shall regard both $M(\mathbf{k})$ and $m(\mathbf{k})$ as arbitrary functions related by

$$m^{-1}(\mathbf{k}) = M^{-1}(\mathbf{k}) + K(\mathbf{k}, M), \quad (\text{IV.105})$$

where the functional $K(\mathbf{k}, M)$ is given explicitly by (IV.28). (IV.105) expresses m as a functional of M . If one solves (IV.104) for M it is obvious that one obtains (IV.24):

$$M(\mathbf{k}) = m(\mathbf{k}) + [m(\mathbf{k})]^2 \sum [\text{all different contracted 1-graphs}]. \quad (\text{IV.106})$$

Equations (IV.105) and (IV.106) are identical with (IV.24) and (IV.27) except that now $m(\mathbf{k})$ is considered to be independent of z .¹⁵

By directly differentiating (IV.104) with respect to M but keeping z constant, we find

$$R_{\mathbf{k}\mathbf{k}'} \equiv \left[\frac{\delta^2 \mathcal{P}(z, M)}{\delta M(\mathbf{k}) \delta M(\mathbf{k}')} \right]_z \\ = -[M(\mathbf{k})]^{-2} \delta_{\mathbf{k}\mathbf{k}'} + \frac{\delta^2 \mathcal{P}'(M)}{\delta M(\mathbf{k}) \delta M(\mathbf{k}')}, \quad (\text{IV.107})$$

which, upon using (IV.105) and (IV.102), can also be written as

$$R_{\mathbf{k}\mathbf{k}'} = \frac{\delta m^{-1}(\mathbf{k})}{\delta M(\mathbf{k}')}.$$

Its inverse matrix R^{-1} is given by

$$(R^{-1})_{\mathbf{k}\mathbf{k}'} = \frac{\delta M(\mathbf{k})}{\delta m^{-1}(\mathbf{k}')}, \quad (\text{IV.108})$$

which can be analyzed in terms of the contracted graphs.

By using (IV.105), the functional derivative

$$[\delta M(\mathbf{k}) / \delta m(\mathbf{k}')]]$$

can be expressed as a sum over graphs. These graphs are obtained by taking any contracted 1-graph and cutting one of its lines open. The result may either be simply two disconnected contracted 1-graphs or a single contracted 2-graph.

We define

$$\mathfrak{N}_2(\mathbf{k}\mathbf{k}') \equiv m^2(\mathbf{k}') \frac{\delta M(\mathbf{k})}{\delta m(\mathbf{k}')} - [M(\mathbf{k})]^2 \delta_{\mathbf{k}\mathbf{k}'}. \quad (\text{IV.109})$$

By differentiating (IV.106) and using the definition (IV.109), we find (after some manipulations)

$$\mathfrak{N}_2(\mathbf{k}, \mathbf{k}') = [m(\mathbf{k})m(\mathbf{k}')]^2 \sum [\text{all different contracted 2-graphs}] \quad (\text{IV.110})$$

in which each graph contributes a term given by (IV.17). The two momenta carried by the two external outgoing (and also the external incoming lines) in these 2-graphs are \mathbf{k} and \mathbf{k}' .

In order to find the relation between $\mathfrak{N}_2(\mathbf{k}, \mathbf{k}')$ and $\langle n_{\mathbf{k}} n_{\mathbf{k}'} \rangle$ we must first establish the following theorems.

Theorem 1.

$$\langle n_{\mathbf{k}} n_{\mathbf{k}'} \rangle - \langle n_{\mathbf{k}} \rangle \langle n_{\mathbf{k}'} \rangle - \langle n_{\mathbf{k}} \rangle \delta_{\mathbf{k}\mathbf{k}'} \\ = \sum_{l=2}^{\infty} [(l-2)!]^{-1} \sum_{1, \dots, l-2} \langle \mathbf{k}, \mathbf{k}', 1, 2, \dots, l-2 \rangle \\ \times |U_l^S| \mathbf{k}, \mathbf{k}', 1, 2, \dots, l-2, \quad (\text{IV.111})$$

¹⁵ Throughout this Appendix, unless stated explicitly, $m(\mathbf{k})$ does not satisfy (IV.16). For example, in the sum (IV.106) and (IV.110) the factor assigned to an internal line is $m(\mathbf{k})$ and not $z[1 - z \exp(-\beta \mathbf{k}^2)]^{-1}$.

where $n_{\mathbf{k}}$ is the occupation number for particles with momentum \mathbf{k} and $\langle \rangle$ refers to statistical averages over a grand canonical ensemble.

Proof.—We consider first a *canonical ensemble* of systems, each containing N identical (but regarded hypothetically as distinguishable) particles. The probability that the first particle has momentum \mathbf{k} and the second particle has \mathbf{k}' is given by

$$(Q_N^S)^{-1} \sum_{3 \dots N} \langle \mathbf{k}, \mathbf{k}', 3, \dots, N | W_N^S | \mathbf{k}, \mathbf{k}', 3, \dots, N \rangle, \quad (\text{IV.112})$$

where

$$Q_N^S = \sum_{1 \dots N} \langle 1, 2, \dots, N | W_N^S | 1, 2, \dots, N \rangle.$$

Since these particles are identical, the same probability must also be given by the average value of

$$[n_{\mathbf{k}}/N][n_{\mathbf{k}'}/(N-1)] \quad \text{if } \mathbf{k} \neq \mathbf{k}',$$

and the average value of

$$[n_{\mathbf{k}}/N][n_{\mathbf{k}}-1/(N-1)] \quad \text{if } \mathbf{k} = \mathbf{k}'.$$

These averages are taken over the canonical ensemble. Upon equating these probabilities and further averaging over a grand canonical ensemble, we obtain

$$\langle n_{\mathbf{k}} n_{\mathbf{k}'} \rangle - \langle n_{\mathbf{k}} \rangle \delta_{\mathbf{k}\mathbf{k}'} \\ = (Q_N^S)^{-1} \sum_{N=2}^{\infty} [(N-2)!]^{-1} z^N \\ \times \sum_{1 \dots N-2} \langle \mathbf{k}, \mathbf{k}', 1, 2, \dots, N-2 \rangle \\ \times |W_N^S| \mathbf{k}, \mathbf{k}', 1, \dots, N-2. \quad (\text{IV.113})$$

Using similar arguments to those used in Appendix B, we can regard W_N^S as a sum over products of U_l^S functions. We distinguish the two different cases: (a) \mathbf{k} and \mathbf{k}' are in the same U_l^S function, and (b) \mathbf{k} and \mathbf{k}' are in two different U_l^S functions. We can then show that the right-hand side of (IV.113) is equal to

$$\sum_{l=2}^{\infty} [(l-2)!]^{-1} z^l \sum_{1 \dots l-2} \langle \mathbf{k}, \mathbf{k}', 1, 2, \dots, l-2 \rangle \\ \times |U_l^S| \mathbf{k}, \mathbf{k}', 1, \dots, l-2 + \langle n_{\mathbf{k}} \rangle \langle n_{\mathbf{k}'} \rangle,$$

where these two terms correspond, respectively, to the above two cases (a) and (b). Thus, Theorem 1 is proved.

Theorem 2.—If

$$m(\mathbf{k}) = z[1 - z \exp(-\beta \mathbf{k}^2)]^{-1}, \quad (\text{IV.16})$$

then

$$z^2 \sum_{l=2}^{\infty} [(l-2)!]^{-1} z^l \sum_{1 \dots l-2} \langle \mathbf{k}, \mathbf{k}', 1, \dots, l-2 \rangle \\ \times |U_l^S| \mathbf{k}, \mathbf{k}', 1, \dots, l-2 \\ = \mathfrak{N}_2(\mathbf{k}, \mathbf{k}') + [M(\mathbf{k}) - z]^2 \delta_{\mathbf{k}\mathbf{k}'}. \quad (\text{IV.113})$$

Proof.—The left-hand side can be regarded as a sum over primary graphs. Graphically, we can represent these sums by first considering a primary 1-graph with external momentum \mathbf{k} . Then we cut one of its internal lines open into two external lines, each labelled by \mathbf{k}' . The resulting form may either: (a') consist of two disconnected primary 1-graphs, or (b') consist of a single primary 2-graph. Thus, we find that the left side of (IV.113) is equal to

$$\delta_{\mathbf{k}\mathbf{k}'} [z^2 \sum (\text{all different primary 1-graphs})^2 + z^4 \sum (\text{all different primary 2-graphs})], \quad (\text{IV.114})$$

in which these two terms correspond to the above two cases (a') and (b'), respectively. (IV.113) now follows by using the identity

$$z^4 \sum (\text{all different primary 2-graphs}) = [m(\mathbf{k})m(\mathbf{k}')]^2 \sum (\text{all different contracted 2-graphs}) \quad (\text{IV.115})$$

provided $m(\mathbf{k})$ is given by (IV.16).

Theorem 3.—If

$$\left[\frac{\delta \mathcal{O}(z, M)}{\delta M(\mathbf{k})} \right]_z = 0, \quad (\text{IV.35})$$

then

$$(R^{-1})_{\mathbf{k}\mathbf{k}'} = -zM(\mathbf{k})\delta_{\mathbf{k}\mathbf{k}'} - z^2 [\langle n_{\mathbf{k}} n_{\mathbf{k}'} \rangle - \langle n_{\mathbf{k}} \rangle \langle n_{\mathbf{k}'} \rangle]. \quad (\text{IV.37})$$

Proof.—We notice that by using (IV.104) and (IV.105), the condition

$$\left[\frac{\delta \mathcal{O}(z, M)}{\delta M(\mathbf{k})} \right]_z = 0$$

is identical with $m(\mathbf{k}) = z[1 - z \exp(-\beta \mathbf{k}^2)]^{-1}$. Theorem 3 now follows immediately by combining (IV.108), (IV.109) with Theorems 1 and 2.

We remark that since the matrix

$$(n_{\mathbf{k}} - \langle n_{\mathbf{k}} \rangle)(n_{\mathbf{k}'} - \langle n_{\mathbf{k}'} \rangle)$$

is a positive matrix and since the average over the grand canonical ensemble is an average with positive probabilities, the resulting matrix

$$\langle n_{\mathbf{k}} n_{\mathbf{k}'} \rangle - \langle n_{\mathbf{k}} \rangle \langle n_{\mathbf{k}'} \rangle$$

must also be a positive matrix. Furthermore, if (IV.35) holds, then

$$M(\mathbf{k}) = z[\langle n_{\mathbf{k}} \rangle + 1],$$

which is positive. Thus R^{-1} and consequently R must be negative matrices if (IV.35) holds.

Next, we will prove that $R_{\mathbf{k}\mathbf{k}'}$ is a negative matrix even though $m(\mathbf{k})$ is not given by $z[1 - z \exp(-\beta \mathbf{k}^2)]^{-1}$, i.e., even though (IV.35) does not hold. We define a function $z_{\mathbf{k}}$,

$$z_{\mathbf{k}}^{-1} \equiv m_{\mathbf{k}}^{-1} + \exp(-\beta \mathbf{k}^2). \quad (\text{IV.116})$$

For arbitrary function $M(\mathbf{k})$ we can, by using (IV.105) and (IV.116), regard $z_{\mathbf{k}}$ as a functional of $M(\mathbf{k})$ and vice versa.

Theorem 4.— $R_{\mathbf{k}\mathbf{k}'}$ is a negative matrix for arbitrary function $M(\mathbf{k})$ provided the corresponding $z_{\mathbf{k}}$ is positive.

Proof.—Let \mathcal{H} be the Hamiltonian of the present problem in terms of the second quantized operators. Instead of the actual grand partition function, we consider a pseudo-partition function defined by

$$\mathcal{Q}' \equiv \text{trace}[\exp(-\beta \mathcal{H}) \prod_{\mathbf{k}} (z_{\mathbf{k}})^{n_{\mathbf{k}}}], \quad (\text{IV.117})$$

Similar to the grand canonical ensemble, we can construct a \mathcal{Q}' -ensemble and regard the probability of finding any system in the ensemble with N particles (identical but considered to be distinguishable) and with a momentum distribution in which the i th particle has \mathbf{k}_i ($i=1, 2, \dots, N$) to be

$$(\mathcal{Q}')^{-1} (N!)^{-1} \langle \mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N | W_N' | \mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N \rangle, \quad (\text{IV.118})$$

where

$$\langle \mathbf{k}_1, \dots, \mathbf{k}_N | W_N' | \mathbf{k}_1, \dots, \mathbf{k}_N \rangle = \sum_P \langle P(\mathbf{k}_1, \dots, \mathbf{k}_N) | W_N | \mathbf{k}_1, \dots, \mathbf{k}_N \rangle \prod_i z_{\mathbf{k}_i}, \quad (\text{IV.119})$$

and W_N is the Boltzmann W_N function given by Eq. (I.4) in paper I.

We can also define $\langle n_{\mathbf{k}} \rangle'$ and $\langle n_{\mathbf{k}} n_{\mathbf{k}'} \rangle'$ as the averages of $n_{\mathbf{k}}$ and $(n_{\mathbf{k}} n_{\mathbf{k}'})$ over a \mathcal{Q}' -ensemble.

In complete analogy with (IV.20), (IV.111), and (IV.113), it can be shown that if we regard $M(\mathbf{k})$ and $\mathcal{H}_2(\mathbf{k}\mathbf{k}')$ as functions of $z_{\mathbf{k}}$ through (IV.106), (IV.110), and (IV.116), then

$$M(\mathbf{k}) = z_{\mathbf{k}} [\langle n_{\mathbf{k}} \rangle' + 1], \quad (\text{IV.120})$$

and

$$\mathcal{H}_2(\mathbf{k}\mathbf{k}') + [M(\mathbf{k}) - z_{\mathbf{k}}]^2 \delta_{\mathbf{k}\mathbf{k}'} = z_{\mathbf{k}} z_{\mathbf{k}'} [\langle n_{\mathbf{k}} n_{\mathbf{k}'} \rangle' - \langle n_{\mathbf{k}} \rangle' \langle n_{\mathbf{k}'} \rangle' - \langle n_{\mathbf{k}} \rangle' \delta_{\mathbf{k}\mathbf{k}'}]. \quad (\text{IV.121})$$

Consequently, by using (IV.108) and (IV.109), we find

$$R_{\mathbf{k}\mathbf{k}'}^{-1} = -z_{\mathbf{k}} M(\mathbf{k}) \delta_{\mathbf{k}\mathbf{k}'} - z_{\mathbf{k}} z_{\mathbf{k}'} [\langle n_{\mathbf{k}} n_{\mathbf{k}'} \rangle' - \langle n_{\mathbf{k}} \rangle' \langle n_{\mathbf{k}'} \rangle']. \quad (\text{IV.122})$$

If $z_{\mathbf{k}} \geq 0$, then the probability (IV.118) is always positive. Consequently, $R_{\mathbf{k}\mathbf{k}'}$ is always a negative matrix.

Thus, we find that the true pressure is given by the *absolute maximum* for $\mathcal{O}(z, M)$ at constant z provided we restrict the variation of $M(\mathbf{k})$ to the domain in which the corresponding $z_{\mathbf{k}}$ is positive.

APPENDIX E

In this Appendix we list some relationships between Υ_l^S , U_l , $U_{l\infty}$, u_l and v_l^S in momentum space.

The U_l and Υ_l^S functions used in this paper are defined for a finite volume Ω . They are related to $U_{l,\Omega}$

(see paper I, Sec. 5] in coordinate space by

$$\begin{aligned} &\langle \mathbf{k}_1', \dots, \mathbf{k}_l' | U_l | \mathbf{k}_1, \dots, \mathbf{k}_l \rangle \\ &= \Omega^{-l} \int \langle \mathbf{r}_1' \dots \mathbf{r}_l' | U_{l,\Omega} | \mathbf{r}_1 \dots \mathbf{r}_l \rangle \\ &\times \exp[i \sum_{\alpha} (\mathbf{k}_{\alpha}' \cdot \mathbf{r}_{\alpha}' - \mathbf{k}_{\alpha} \cdot \mathbf{r}_{\alpha})] \prod_{\alpha} d^3 r_{\alpha} d^3 r_{\alpha}'. \quad (\text{IV.123}) \end{aligned}$$

The $U_{l,\Omega}$ functions in momentum space are defined by

$$\begin{aligned} &\langle \mathbf{k}_1', \dots, \mathbf{k}_l' | U_{l,\Omega} | \mathbf{k}_1, \dots, \mathbf{k}_l \rangle \\ &= (8\pi^3)^{-l} \int \langle \mathbf{r}_1', \dots, \mathbf{r}_l' | U_{l,\Omega} | \mathbf{r}_1, \dots, \mathbf{r}_l \rangle \\ &\times \exp[i \sum_{\alpha} (\mathbf{k}_{\alpha}' \cdot \mathbf{r}_{\alpha}' - \mathbf{k}_{\alpha} \cdot \mathbf{r}_{\alpha})] \prod_{\alpha} d^3 r_{\alpha} d^3 r_{\alpha}', \quad (\text{IV.124}) \end{aligned}$$

where $U_{l,\Omega}$ in the coordinate space was defined in paper I. Thus if we define u_l by Eq. (I.54), then as $\Omega \rightarrow \infty$,

$$\begin{aligned} &[\Omega/(8\pi^3)]^{l-1} \langle \mathbf{k}_1', \dots, \mathbf{k}_l' | U_l | \mathbf{k}_1, \dots, \mathbf{k}_l \rangle \\ &\rightarrow \langle \mathbf{k}_1', \dots, \mathbf{k}_l' | u_l | \mathbf{k}_1, \dots, \mathbf{k}_l \rangle \delta_{\mathbf{K}, \mathbf{K}'}, \quad (\text{IV.125}) \end{aligned}$$

where $\mathbf{K} = \sum \mathbf{k}_{\alpha}$ and $\mathbf{K}' = \sum \mathbf{k}_{\alpha}'$. Similarly we find, as $\Omega \rightarrow \infty$,

$$\begin{aligned} &[\Omega/(8\pi^3)]^{l-1} \langle \mathbf{k}_1', \dots, \mathbf{k}_l' | \Upsilon_l^S | \mathbf{k}_1, \dots, \mathbf{k}_l \rangle \\ &\rightarrow \delta_{\mathbf{K}, \mathbf{K}'} \langle \mathbf{k}_1', \dots, \mathbf{k}_l' | v_l^S | \mathbf{k}_1, \dots, \mathbf{k}_l \rangle, \quad (\text{IV.126}) \end{aligned}$$

where v_l^S is defined by (IV.54). Both u_l and v_l^S are independent of volume.

Some explicit forms of Υ_l^S and v_l^S for hard spheres have been given in papers II and III.

Theory of Fluorescence Time Constant Measurements in Liquid and Rigid Solutions*

HARTMUT KALLMANN

Department of Physics, New York University, New York, New York

(Received June 16, 1959)

Formulas are derived for the dependence of fluorescence upon time for the case when energy transfer from the solvent to the solute is involved. Three cases are considered: excitation by single fast particles, excitation by one burst of particles during a given period, and periodic excitation. One important point is that in the rise and decay of fluorescence from a burst of particles, it is the difference of two exponential functions and not their sum which occurs. The results are compared with the experiments of Burton and Dreeskamp, of Swank and Buck, and of Knau. These experiments are in general accordance with the derived formulas.

A THEORY of light emission from a liquid or rigid solution which is energized by a fast particle has been given by Brucker and Kallmann.¹ It shows that in a solution containing a single solute and solvent where the fluorescence is emitted mainly by the solute, the light emission, I , varies with time according to the formula

$$I = N\alpha\kappa\frac{\tau_s}{\tau_s - \tau_u} \left[\exp\left(-\frac{t}{\tau_s}\right) - \exp\left(-\frac{t}{\tau_u}\right) \right]. \quad (1)$$

This formula holds if the solute is excited via energy transfer only. N is the total number of excited molecules of the bulk material, $\alpha\kappa$ is the probability per unit time that energy is transferred to the solute, and τ_u is the decay time of the solute as measured under direct light excitation (not via energy transfer). $1/\tau_s = 1/\tau_0 + \alpha\kappa$, where τ_0 is the time constant of the solvent in the absence of solute. κ is the product of the quantum efficiency of the solute when directly excited by light and the efficiency of energy transfer. According to recent measurements, this latter efficiency is close to

one.² Often, however, the solution is not energized by a single particle but by a burst of particles during a period of time, T , as is the case in the experiments of Burton and Dreeskamp³ and Swank and Buck⁴; or, the solution is continuously excited with an excitation intensity varying with the period ω . This is the case in the experiments of Knau.⁵

Formula (1) cannot be applied directly to these cases, but the theory can be extended by a straightforward procedure to include the effect of a burst of particles or of periodic excitation.

If the excitation is extended over a period of T seconds, then the following formulas for the light emission are obtained:

$$\begin{aligned} t < T: \quad I = & \frac{N_0\alpha\kappa\tau_s}{T(\tau_s - \tau_u)} \left\{ \tau_s \left[1 - \exp\left(-\frac{t}{\tau_s}\right) \right] \right. \\ & \left. - \tau_u \left[1 - \exp\left(-\frac{t}{\tau_u}\right) \right] \right\}, \quad (2) \end{aligned}$$

² Brown, Furst, and Kallmann, Discussions Faraday Soc. (to be published).

³ M. Burton and H. Dreeskamp, Discussions Faraday Soc. (unpublished).

⁴ W. L. Buck and R. K. Swank, Argonne National Laboratory, Physics Division, Summary Report, 1958 (unpublished).

⁵ H. Knau, Z. Naturforsch. **12a**, 881 (1957).

* This work was supported by the Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey.

¹ G. Brucker and H. Kallmann, Phys. Rev. **108**, 1122 (1957).