

LECTURES ON GRAPH THEORY IN STATISTICAL PHYSICS,

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## I. INTRODUCTION

In these lectures we are going to discuss the use of graph theoretical techniques in the study of the equilibrium statistical mechanics of classical systems. The basic theory was developed largely during the 1950's in an attempt to develop approximate theories of dense fluids and a large fraction of the development of liquid state physics since has been concerned with the solution of the integral equations which came from the approximate theories<sup>[1-10]</sup>. An excellent review of the basic theory was written by Stell and published in 1964<sup>[11]</sup>. We shall attempt to use the notation of Stell consistently in these lectures.

Since the early 1960's, the use of graph theory in deriving the standard dense fluid approximations (such as Percus-Yevick and hypernetted chain) has declined and been replaced by techniques of functional differentiation<sup>[12-15]</sup>. It is often claimed (and possibly rightly so) that the functional differentiation techniques give more physical insight into the nature of the approximations developed than do the graph theoretical techniques. However, as liquid state physics has progressed it has become clear that simple application of standard approximations is not a particularly useful way to proceed. In particular, "thermodynamic perturbation theories" have been developed which give good agreement with thermodynamic experimental results. Other new approximate dense liquid theories have also been developed. A feature of these newer theories is that the derivations of many of them were first published in forms using graph theoretical techniques. The optimized cluster expansion of

Anderson, Chandler and Weeks<sup>[16]</sup> is a typical example. A whole class of newer problems, those of molecular fluids, has also required the development of new approximations. Again, this development has been via graphical techniques at the first. The first analysis of the nature of the RISM approximation for molecular fluids, for example, was carried out by graphical techniques<sup>[17]</sup>. Much of the development of theories of the dielectric constant of polar and non-polar fluids has been by graphical techniques<sup>[18]</sup>, and the difficult problems of divergences associated with long-range electrostatic potentials are often most clearly phrased in a graphical context. Finally we would mention the development of thermodynamic perturbation theories for molecular fluids where there are many different approaches. Most of them may be derived by graphical techniques, which are particularly useful for choosing one method as more quickly convergent than others<sup>[19]</sup>.

In many of these cases the original derivations have been superseded by derivations using functional differentiation, and the new derivations have made the nature of the approximations more clear. However, the rather more direct link between graph theory and physical intuition makes it appear that while graph theory may be an inelegant tool in developing approximations in dense fluid physics, it is a successful tool. Thus a solid grasp of the techniques used is an important part of a theoreticians toolkit, and this provides the main reason for giving these lectures.

In the next section we define the statistical mechanical quantities we shall be discussing, the idea of a graph and of functional

differentiation as they are used in statistical mechanics, and show some of the connections between the two methods. In later sections we derive the fugacity and density expansions for the pressure and the correlation functions and prove two "replacement theorems". These are theorems which are used in the technique called "topological reduction" by Stell, where a sum over one set of graphs is replaced by a sum over a smaller class of graphs. A proof of the convergence of the fugacity expansion for the pressure in a finite circle of the complex fugacity plane is derived by graph theoretical methods and the Percus-Yevick and hypernetted chain approximations are derived. We then give a brief introduction to the graphical methods used in the study of systems with electrostatic interactions. Finally we discuss the way graphical techniques are used in the development of some of the newer perturbation theories, demonstrating these ideas with an example: the Weeks, Chandler and Anderson theory.

We hope that this probably rather personal view of the place of graph theoretic techniques in modern theories of the liquid state may be of some use to apprentice workers in the field. We thank those students and colleagues whose attentive ears made the lectures possible in the first place.



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## II DEFINITIONS.

### (a) Statistical Mechanics.

We consider a system of  $N$  particles constrained to lie in a region  $\Omega$  of volume  $|\Omega|$  and whose surface area,  $|\partial\Omega|$  is small compared with  $|\Omega|$ . We write the coordinates of the  $i^{\text{th}}$  particle as  $(i)$ , the symbol representing both the centre of mass coordinates and interval coordinates such as orientation or vibration coordinates. THE CANONICAL PARTITION FUNCTION for the system is

$$Z_N(\Omega, T) = \frac{1}{N!} \int_{\Omega} d(1) \dots \int_{\Omega} d(N) \exp[-\beta V(1), \dots, (N))] \quad (2.1)$$

where  $\beta = 1/kT$ ,  $k$  is Boltzmann's constant,  $T$  the absolute temperature and  $V(1, \dots, N)$  the potential energy of the particle configuration  $\{(1), \dots, (N)\}$ . In these notes we shall assume  $V$  to be a sum of single particle and pairwise interactions:

$$V(1), \dots, (N) = \sum_{i=1}^N \phi_1(i) + \sum_{1 \leq i < j \leq N} \phi_2(i, j). \quad (2.2)$$

The one particle potential  $\phi_1$  may include the effects of the walls of the container, for example. Another example is, of course, the potential of the gravitational field of the earth, which is responsible for such important effects as phase separation in liquid-gas phase transitions. Equation (2.2) represents the assumptions that three and more particle potentials are unimportant in statistical mechanics. The recent calculations of Barker et al. of the third virial coefficient of

argon<sup>[20]</sup> indicate that even in simple real systems (i.e. a monomolecular system with spherically symmetric potentials), the assumption of no interactions of order higher than pairwise can be grossly inaccurate. The major attraction of assuming the potential energy to have the form in equation (2.2) is that while it seems to include enough physics to cover all physical phenomena, it makes the theory we are about to develop rather more simple to write down and manipulate. It is possible to develop this theory with many particle interactions included but for dense fluids it seems simpler to use an effective two particle potential.

The GRAND CANONICAL PARTITION FUNCTION may be written

$$\Xi(z, \Omega, T) = \sum_{k=0}^{\infty} z^k Z_k(\Omega, T) \quad (2.3)$$

where the fugacity  $z$  is given by

$$z = e^{-\beta\mu} \lambda^{-3} \quad (2.4)$$

with  $\lambda$  the thermal deBroglie wave length for the particles and  $\mu$  the chemical potential of the system. The  $k = 0$  term in equation (2.3) is 1 by definition.

We may define CANONICAL AND GRAND CANONICAL DISTRIBUTION FUNCTIONS. The  $k$ -particle canonical distribution function is

$$n_k^{(N)}((1), \dots, (k)) = \frac{N!}{(N-k)!} \int_{\Omega} d(k+1) \dots \int_{\Omega} d(N) D_N((1), \dots, (N)) \quad (2.5)$$

where

$$D_N((1), \dots, (N)) = \frac{1}{N! Z_N(\Omega, T)} \exp[-\beta V((1), \dots, (N))] \quad (2.6)$$

The k-particle grand canonical distribution function is

$$\rho_k((1), \dots, (N)) = \frac{1}{\mathcal{Z}} \sum_{N \geq k} n_k^{(N)}((1), \dots, (k)) z_N^N(\Omega, T). \quad (2.7)$$

We now see the use of functional differentiation: these correlation functions, which describe the microscopic structure of systems, are in fact functional derivatives of the partition functions.

#### (b) Functional Differentiation and its use in Statistical Mechanics.

We now review the definitions of functional derivatives. A useful reference on functional differentiation ~~is~~ the first<sup>[21]</sup> since it has been republished in paperback. A useful review of the techniques as used in statistical mechanics has been given by Baxter<sup>[22]</sup>. We begin by considering  $y_1, \dots, L\{x\}$  to be a function of  $L$  sets of position coordinates  $(1), \dots, (L)$  and a functional of the function  $x$  which we consider a function of an  $(L+1)^{\text{th}}$  set of position coordinates. We may ask what change in  $y$  occurs as a result of a small change in the function  $x(L+1)$ . First we consider the function  $x$  to be approximated by a step function and hence represented by a table of its values  $\{x(L+1)_i\}_{i=1}^P$  at  $P$  values  $\{(L+1)_i\}_{i=1}^P$  of its argument  $(L+1)$ . If we change  $x$  to  $x + \epsilon$ , then the values of the function in the table will change. We may consider the functional  $y$  as a function of the  $P$  variables  $\{x(L+1)_i\}_{i=1}^P$  and so the change in  $x$  will result in a change

$$y_1, \dots, L\{x + \epsilon\} - y_1, \dots, L\{x\} = \sum_{i=1}^P \epsilon((L+1)_i) \frac{\partial y_1, \dots, L\{x\}}{\partial x((L+1)_i)}.$$

As we take  $P \rightarrow \infty$ , we may expect the sum in this equation to turn into

an integral. Thus we try to make the functional Taylor series expansion

$$y_{1,\dots,L}\{x + \varepsilon\} = y_{1,\dots,L}\{x\} + \int d(L+1) \varepsilon_{L+1} y_{1,\dots,L/L+1}^{(1)}\{x\} \\ + \frac{1}{2!} \int d(L+1) \int d(L+2) \varepsilon_{L+1} \varepsilon_{L+2} y_{1,\dots,L/L+1,L+2}^{(2)}\{x\} + \dots \quad (2.8)$$

This attempt is, however, a little glib, since the objects  $y_{1,\dots,L/L+1,\dots,L+M}^{(M)}\{x\}$  are not unique. The addition to them of suitable antisymmetric functions of  $(L+1), \dots, (L+M)$  for  $M \geq 2$  leaves the expansion (2.8) unchanged. We impose a unique definition by insisting that  $y^{(M)}$  be symmetric in its  $M$  extra arguments. We write this symmetrized form as

$$y_{1,\dots,L/L+1,\dots,L+M}^{(M)}\{x\} = \frac{\delta^M y_{1,\dots,L}\{x\}}{\delta x_{L+1} \dots \delta x_{L+M}} \quad (2.9)$$

and call it the  $M^{\text{th}}$  functional of  $y$ . In practice, the functional derivative works in the same way as an ordinary derivative, e.g.

$$y_{1,\dots,L/L+1,\dots,L+M}^{(M)}\{x\} = \frac{\delta}{\delta x_{L+M}} \left\{ y_{1,\dots,L/L+1,\dots,M-1}^{(M-1)}\{x\} \right\} \quad (2.10)$$

To use the idea of functional differentiation in statistical mechanics, we first define

$$z_1(i) = z \exp[-\beta \phi_1(i)] \quad (2.11)$$

so that (2.3) may be written

$$\Xi(z_1) = \sum_{N=0}^{\infty} \frac{1}{N!} \int d(1) \dots \int d(N) \exp[-\beta \sum_{1 \leq i < j \leq N} \phi_2(i,j)] \prod_{i=1}^N z_1(i) \quad (2.12)$$

We then have

$$\begin{aligned} \square(z_1 + \delta z_1) &= \sum_{N=0}^{\infty} \frac{1}{N!} \int d(1) \dots d(N) \exp[-\beta \sum_{1 \leq i < j \leq N} \phi_2(i, j)] \prod_{i=1}^N [z_1(i) + \delta z_1(i)] \\ &= \sum_{N=0}^{\infty} \left\{ \sum_{M=0}^{\infty} \frac{1}{M!(N-M)!} \int d(1) \dots d(N) \delta z_1(1) \dots \delta z_1(M) \exp[-\beta \sum_{i < j} \phi_2(i, j)] \prod_{i=1}^N z_1(i) \right. \\ &\quad \left. \times \left[ \prod_{j=1}^M z_1(j) \right]^{-1} \right\}, \end{aligned}$$

using the symmetry of the integrand with respect to  $(1), \dots, (N)$  to derive the second line from the first. We may now factorize out the  $M = 0$  term to find

$$\begin{aligned} \square(z_1 + \delta z_1) &= \square(z_1) \left\{ 1 + \sum_{M=1}^{\infty} \frac{1}{M!} \int d(1) \dots d(M) \delta z_1(1) \dots \delta z_1(M) \right. \\ &\quad \times \sum_{N=M}^{\infty} \frac{1}{\square(z_1)} \frac{1}{(N-M)!} \int d(M+1) \dots d(N) \\ &\quad \left. \exp[-\beta \sum_{i < j} \phi_2(i, j)] \prod_{i=1}^N z_1(i) / \prod_{j=1}^M z_1(j) \right\} \\ &= \square(z_1) \left\{ 1 + \sum_{M=1}^{\infty} \frac{1}{M!} \int d(1) \dots d(M) \frac{\delta z_1(1) \dots \delta z_1(M)}{z_1(1) \dots z_1(M)} P_M((1), \dots, (M)) \right\}. \end{aligned}$$

Comparing this result with equation (2.8) we see

$$P_M((1), \dots, (M)) = \frac{z_1(1) \dots z_1(M)}{\square(z_1)} \frac{\delta^M \square(z_1)}{\delta z_1(1) \dots \delta z_1(M)}. \quad (2.13)$$

We now introduce the URSELL CLUSTER FUNCTIONS  $u_k((1), \dots, (k))$

by the definition

$$P_M((1), \dots, (M)) = \sum_P \prod_{\alpha \in P} u_{n_\alpha}((i_1), \dots, (i_{n_\alpha})) \quad (2.14)$$

where the sum is over all partitions  $P$  of the set  $\{1, \dots, M\}$  and the product for each partition  $P$  is over all the subsets  $\alpha$  of  $P$ , the  $\alpha^{\text{th}}$  subset having elements  $i_1, \dots, i_{n_\alpha}$ . There is only one partition of the set  $\{1\}$  so that

$$P_1(1) = u_1(1) . \quad (2.15)$$

The set  $\{1, 2\}$  may be partitioned in two ways:  $\{1, 2\}$  or  $\{1\}, \{2\}$ . The two particle Ursell cluster function is then

$$P_2(1, 2) = u_2(1, 2) + u_1(1) u_1(2) . \quad (2.16)$$

For  $M = 3$ , we have the partitions  $\{1, 2, 3\}; \{1\}, \{2, 3\}; \{1, 2\}, \{3\}; \{1, 3\}, \{2\}; \{1\}, \{2\}, \{3\}$ , and thus have

$$\begin{aligned} p_3(1, 2, 3) &= u_3(1, 2, 3) + u_1(1)u_2(2, 3) + u_1(3) u_2(1, 2) \\ &+ u_1(2) u_2(1, 3) + u_1(1)u_1(2)u_1(3) \end{aligned} \quad (2.17)$$

and so on.

Since functional derivatives work in the same way as ordinary derivatives, we have the result

$$\frac{\delta \log \Xi}{\delta z_1(i)} = \frac{1}{\Xi} \frac{\delta \Xi}{\delta z_1(i)} . \quad (2.18)$$

If we use (2.18) to write  $\delta^M \log \Xi / \delta z_1(1) \dots \delta z_1(M)$  in terms of



functional derivatives of  $\Xi$  we see from (2.14) that

$$u_M(\langle 1 \rangle, \dots, \langle M \rangle) = z_1(\langle 1 \rangle) \dots z_1(\langle M \rangle) \frac{\delta^M \log \Xi}{\delta z_1(\langle 1 \rangle) \dots \delta z_1(\langle M \rangle)} \quad (2.19)$$

We may define several other useful correlation functions. They are

$$g_M(\langle 1 \rangle, \dots, \langle M \rangle) = \frac{\rho_M(\langle 1 \rangle, \dots, \langle M \rangle)}{\rho_1(\langle 1 \rangle) \dots \rho_1(\langle M \rangle)} \quad (2.20)$$

and for  $M \geq 2$

$$h_M(\langle 1 \rangle, \dots, \langle M \rangle) = \frac{u_M(\langle 1 \rangle, \dots, \langle M \rangle)}{\rho_1(\langle 1 \rangle) \dots \rho_1(\langle M \rangle)} \quad (2.21)$$

while for  $M = 1$

$$h_1(\langle 1 \rangle) = \log[u_1(\langle 1 \rangle)/z_1(\langle 1 \rangle)] \quad (2.22)$$

For the two particle functions we have

$$h_2(\langle 1, 2 \rangle) = g_2(\langle 1, 2 \rangle) - 1 \quad (2.23)$$

For the ideal gas, equations (2.20) and (2.7) show that  $g_2(\langle 1, 2 \rangle) = 1$ .

Equation (2.23) then shows that  $h_2(\langle 1, 2 \rangle)$  is a measure of the departure of a system from ideal behaviour.

There is one further correlation function we shall require:  
the <sup>N</sup>ORSTEIN-ZERNIKE DIRECT CORRELATION FUNCTION is defined as the solution of the integral equation

$$h_2(\langle 1, 2 \rangle) = c(\langle 1, 2 \rangle) + \int d\langle 3 \rangle c(\langle 1, 3 \rangle) \rho_1(\langle 3 \rangle) h_2(\langle 3, 2 \rangle) \quad (2.24)$$

An alternative function definition of  $c(\langle 1, 2 \rangle)$  is

$$c(1,2) = \frac{\delta}{\phi_1(2)} \log[\delta \log \psi/\delta z_1(1)] \quad (2.24)$$

We shall show, in section vii that this functional definition is the same as the definition via the Ornstein-Zernike equation (2.24).

### (C) Graphical Definitions.

In our graphical definitions we use the definitions of Stell, and do not list any of the many alternative names which most of the defined objects have. A LINEAR GRAPH is a collection of circles, between some pairs of which there are lines called bonds. Two circles are ADJACENT if they are joined by a bond. A PATH is a sequence of adjacent circles joined by bonds. Two paths between the circles  $z_1$  and  $z_2$  are INDEPENDENT if they have no intermediate circles in common. A graph is CONNECTED if any pair of circles in the graph are joined by a path. There are two types of circles: WHITE CIRCLES, (which carry a label and whose coordinates are not integrated out) and BLACK CIRCLES (which are unlabelled and whose coordinates are always integrated over). If there are at least  $n$  independent paths between any pair of circles in a graph then it is AT-LEAST- $n$ -TUPLY-CONNECTED. In general, a graph consists of several disconnected COMPONENTS. A component is a maximal connected subgraph. A MAXIMAL subgraph with a property is the subgraph with the property which is properly contained in no other subgraph with the property. A MINIMAL subgraph with some property properly contains no other subgraph with the property. In a SIMPLE GRAPH, there is at most one bond between any pair of circles.

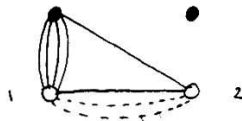
With each graph we associate two objects: an integral and a symmetry number. The most general integral necessary for our purposes is of the form

$$\int d(n+1) \dots \int d(N) \left\{ \prod_s \prod_a [B_a(i,j)] m_a(i,j) \right\} \left\{ \prod_{1 \leq i \leq n} \gamma_1(i) \right\} \left\{ \prod_{n+1 \leq i \leq N} \gamma_2(i) \right\}. \quad (2.26)$$

Equation (2.26) is the integral associated with an  $N$  circle graph in which  $n$  of the circles are white and labelled  $1, \dots, n$  while the other  $N-n$  circles are black. With each black circle there is associated a function  $\gamma_2(i)$  and with each white circle a function  $\gamma_1(j)$ . The set  $S$  is the set of pairs of circles  $(i,j)$  between which there are bonds. The product over  $a$  is over types of bonds and  $m_a(i,j)$  is the number of  $a$ -type bonds between  $(i,j)$ . With each  $a$ -type bond we associate a function  $B_a(i,j)$  which has the property  $B_a(i,j) = B_a(j,i)$ . For the (simple) case of the complete  $N$  circle graph, one integral would be

$$N! Z_N = \int d(1) \dots \int d(N) \exp[-\beta \sum_{i < j} \phi_2(i,j)].$$

$S$  is the set of  $N(N+1)/2$  pairs  $(i,j)$ , there is only one type of bond, with,  $B_1(i,j) = \exp[-\beta \phi_2(i,j)]$ ,  $m_1(i,j) = 1 \forall (i,j)$  and  $\gamma_1(i) = \gamma_2(i) \forall i$ . Another example is



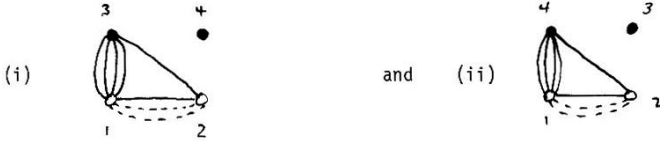
which has the associated integral

$$\int d(3) \int d(4) B_1(1,3)^4 B_1(1,2) B_1(2,3) B_2(1,2)^2 \gamma_1(1) \gamma_1(2) \gamma_2(3) \gamma_2(4) . \quad (2.27)$$

Each integral corresponds to the graph with which it is associated times the factor

$$v = \sigma \prod_a \prod_{i,j} \{m_a(i,j)!\} . \quad (2.28)$$

The number  $\sigma$  is the symmetry number of the graph, which is the order of the automorphism group of the graph. To define this group we make a dummy labelling of the black circles of the graph. The group is the group of permutations of the dummy labels of the black circles which leaves unchanged the adjacency of the relabelled graph. This is, the values of  $m_a(i,j)$  in the original labelling, and in the permuted labelling are the same for all  $i,j$  and  $a$  in the graph. For the graph drawn above there are two labellings of the graph



In (i), 3 is bonded to 2, but not in (ii). Hence the automorphism group contains only the identity and  $\sigma = 1$ .  $m_1(1,2) = 1$ ;  $m_1(2,3) = 1$ ,  $m_1(3,1) = 4$  while  $m_2(1,2) = 2$ . Thus

$$v = 1 \times (1! \cdot 1! \cdot 4!) \times (2!) = 48 .$$

A graph with integral  $I$  and number  $v$  corresponds to the term  $I/v$ .

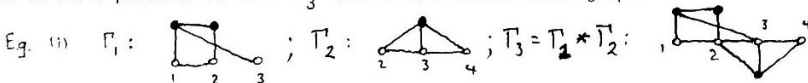
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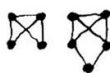
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### III. PRELIMINARY THEOREMS

In this section we prove the "PRODUCT THEOREM" which relates sums over connected graphs to sums over disconnected graphs. We also interpret functional derivatives of graphs as graphical expressions. When we speak of a graph (or a sum of graphs), we may mean either the graph as drawn, or the term corresponding to it (or the sum of such terms). We won't make the distinction very often, trusting that the meaning is obvious from the context.

We now introduce the idea of a PRODUCT OF GRAPHS. We let  $\Gamma_1$  be a connected graph with  $n$  white 1-circles. A 1-circle is a circle whose function  $\gamma$  is unity (see (2-26)). We label these circles  $i_1, \dots, i_n$ . We let  $\Gamma_2$  be a connected graph with  $m$  white 1-circles labelled by  $j_1, \dots, j_m$ . We now consider the white circles labelled by  $k_1, \dots, k_Q$  where  $k_1, \dots, k_Q$  are the labels common to  $\{i_1, \dots, i_n\}$  and  $\{j_1, \dots, j_m\}$ . The product of  $\Gamma_1$  and  $\Gamma_2$ , denoted  $\Gamma_1 * \Gamma_2$ , is defined as the graph  $\Gamma_3$  containing the white circles  $k_1, \dots, k_Q$  and such that the removal of the circles labelled  $k_1, \dots, k_Q$  separates the graph into two pieces, one piece being  $\Gamma_1$  minus the white circles  $k_1, \dots, k_Q$  and the other piece being  $\Gamma_2$  minus the white circles  $k_1, \dots, k_Q$ . If we remove the graph ( $\Gamma_2$  minus its white points) from  $\Gamma_3$  we get  $\Gamma_1$ , if we remove the graph ( $\Gamma_1$  minus its white points) from  $\Gamma_3$  we get  $\Gamma_2$ . We say that  $\Gamma_3$  is  $\Gamma_1$  and  $\Gamma_2$  connected in parallel at the points  $k_1, \dots, k_Q$ . Note that if either  $\Gamma_1$  or  $\Gamma_2$  contains no white circles, it is still possible to form  $\Gamma_3$  but it is a disconnected graph.



(ii)  $\Gamma_1$  :  ;  $\Gamma_2$  :  ;  $\Gamma_3 = \Gamma_1 * \Gamma_2$  : .

If  $I_1$  is the integral corresponding to  $v_1 \Gamma_1$  and  $I_2$  is the integral

corresponding to  $v_2 \Gamma_2$  then the product  $I_1 I_2$  does not necessarily correspond to  $v_1 v_2 (\Gamma_1 * \Gamma_2)$ . The integral associated with  $\Gamma_3 = \Gamma_1 * \Gamma_2$  is certainly  $I_1 I_2$ , but there is no guarantee that the symmetry number  $v_3$  of  $\Gamma_3$  is equal to  $v_1 v_2$ . However, despite the fact that  $I_1 I_2 / v_1 v_2$  may not equal  $\Gamma_1 * \Gamma_2$ , we can prove the following theorem. It is basic to the derivation of the fugacity expansions in the next section and crops up frequently in subsequent work.

#### PRODUCT THEOREM

Let  $G$  be a set of distinct connected graphs  $\Gamma_1, \Gamma_2, \dots, \Gamma_j, \dots$ , each consisting of some or no black circles, some or no white 1-circles and some or no bonds. We assume that NO products of members of  $G$  are members of  $G$ . Let  $F$  be the set of all graphs in  $G$  and all possible products of graphs in  $G$  (including multiple products). The product theorem then states

$$\left\{ \begin{array}{l} \text{THE FUNCTION REPRESENTED BY THE SUM} \\ \text{OF ALL GRAPHS IN THE SET } F \end{array} \right\} = \exp \left\{ \begin{array}{l} \text{THE FUNCTION REPRESENTED BY} \\ \text{THE SUM OF ALL GRAPHS IN } G \end{array} \right\}^{-1}. \quad (3)$$

PROOF:

A typical graph in  $F$  has the form

$$\phi_i = \Gamma_1 * \Gamma_2 * \Gamma_3 \dots * \Gamma_n$$

so that the integral associated with the graph has the form

$$\phi_i = I_1^{p_1} I_2^{p_2} \dots I_n^{p_n} / v_{\phi_i} \quad (3.2)$$

where  $v_{\phi_i}$  is the factor associated with  $\phi_i$  and  $I_i = v_{\Gamma_i} \Gamma_i$ . Because of the construction of product graphs, there is no bond from any black circle in any graph in the product to a black circle in another graph in the product. Thus the only difference between  $v_{\phi_i}$  and  $\prod_{i=1}^n [(v_{\Gamma_i})^{p_i}]$  is associated with the way the  $p_i$  graphs  $\Gamma_i$  are ordered in the product graph. We can order them in  $\phi_i!$  ways so that

$$v_{\phi_i} = \left[ \prod_{i=1}^n p_i! \right] \prod_{i=1}^n [(v_{\Gamma_i})^{p_i}] \quad (3.3)$$

If we now sum equation (3.2) over all graphs in the collection  $F$  and use equation (3.3), we see that

$$\exp \left\{ \frac{I_1}{v_{\Gamma_1}} + \frac{I_2}{v_{\Gamma_2}} + \dots + \frac{I_j}{v_{\Gamma_j}} + \dots \right\} - 1 = \exp \left\{ \Gamma_1 + \Gamma_2 + \dots + \Gamma_j + \dots \right\} - 1 \quad (3.4)$$

The left hand side of this equation is the right hand side of equation (3.1) and the right hand side of (3.4) can be shown to be the left hand side of (3.1) by expanding the exponential. Hence we have proven the product theorem.

We now proceed to give two results on functional derivations of graphs.

Let  $\Gamma$  be a connected graph consisting of bonds and black circles such that some (or none) of the circles are  $\gamma$ -circles and some (or none) of the bonds are  $B$  bonds. Then we have



$$\frac{\delta^n \Gamma}{\delta \gamma(1) \dots \delta \gamma(n)} = \left\{ \begin{array}{l} \text{THE SUM OF ALL THE DISTINCT GRAPHS THAT ARE} \\ \text{OBTAINED FROM } \Gamma \text{ BY CHANGING } n \text{ BLACK } \gamma\text{-} \\ \text{CIRCLES TO WHITE 1-CIRCLES LABELLED } 1, \dots, n \\ \text{RESPECTIVELY.} \end{array} \right. \quad (3.5)$$

If  $n$  exceeds the number of black  $\gamma$ -circles, then the derivative is naturally zero. We also have

$$\frac{\delta \Gamma}{\delta B(i,j)} = \frac{1}{2} \left\{ \begin{array}{l} \text{THE SUM OF ALL THE DISTINCT GRAPHS THAT ARE} \\ \text{OBTAINED FROM } \Gamma \text{ BY REMOVING A B-BOND AND} \\ \text{CHANGING THE TWO CIRCLES AT EITHER END OF } B \\ \text{FROM BLACK CIRCLES TO WHITE CIRCLES LABELLED} \\ i \text{ AND } j \text{ RESPECTIVELY.} \end{array} \right. \quad (3.6)$$

We use these results in the succeeding sections. Their proof is not difficult starting from equation (2.26) and the definition of functional differentiation. A simple example of (3.5) might be

$$\frac{\delta}{\delta \gamma(1)} \left( \text{graph with 2 black circles and 1 white circle} \right) = \left( \text{graph with 1 black circle and 1 white circle} \right) + \left( \text{graph with 2 black circles and 1 white circle} \right),$$

where all the black circles in the original graph are  $\gamma_1$ -circles.

#### IV. FUGACITY EXPANSIONS

From equation (2.12) we can see that

$$\Xi = 1 + \left\{ \begin{array}{l} \text{THE SUM OF ALL THE COMPLETE SIMPLE GRAPHS WITH} \\ \text{ALL BLACK } z_1\text{-CIRCLES AND } e\text{-BONDS} \end{array} \right. \quad (4.1)$$

The complete simple graph of N-circles is the graph of N circles in which every pair of circles is joined by one and only one bond. An e-bond may be written

$$e(i,j) = e^{-\frac{1}{kT} \phi_2(i,j)} \quad (4.2)$$

and the  $i^{\text{th}}$  black circle has the function

$$z_1(i) \approx z e^{-\frac{1}{kT} \phi_1(i)} \quad (4.3)$$

We can rewrite (4.1) pictorially as

$$= 1 + \bullet + \bullet\text{---}\bullet + \text{triangle} + \dots$$

However, this is not a useful expansion because since  $e(i,j) \rightarrow 1$  as the distance  $r(i,j)$  between  $i$  and  $j$  gets large, the  $n$  circle term in (4.1) is proportional to  $|\Omega|^n$ . The series in fact diverges.

However, if we use the bond

$$f(i,j) = e(i,j) - 1 \quad (4.4)$$

then  $f(i,j) \rightarrow 0$  as  $r(i,j) \rightarrow \infty$ . Using (4.4) in (4.1) we find

$$\Xi = 1 + \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT SIMPLE GRAPHS CONSISTING} \\ \text{OF BLACK } z_1\text{-CIRCLES AND SOME OR NO } f\text{-BONDS.} \end{array} \right. \quad (4.5)$$

$$= 1 + \bullet + \bullet + \bullet + \bullet + \bullet + \bullet + \bullet + \bullet + \bullet + \dots$$

We may now use the product theorem to obtain an expansion for  $\log \Xi$ .

We find

$$\log \Xi = \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT CONNECTED SIMPLE GRAPHS} \\ \text{COMPOSED OF BLACK } z_1\text{-CIRCLES AND SOME OR NO} \\ \text{f-BONDS.} \end{array} \right. \quad (4.6)$$

$$= \bullet + \bullet + \bullet + \bullet + \dots$$

The integrand of each graph in this expansion is given in terms of the coordinates of one circle and the coordinates of all the other circles relative to the first circle. The integration over the coordinates of the first circle then gives, for homogeneous systems, a factor  $|\Omega|$ . Equation (4.6) is the fugacity expansion of  $|\Omega|$  times the pressure. We can now use equations (3.5) and (3.6) and the functional definitions of the correlation functions. We have

$$u_M((1), \dots, (M)) = \left\{ \prod_{1 \leq i \leq M} z_1(i) \right\} \frac{\delta^M \log \Xi}{\delta z_1(1) \dots \delta z_1(M)}$$

(equation (2-19)). Using (3.5) we obtain

$$u_K((1), \dots, (K)) = \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT CONNECTED SIMPLE} \\ \text{GRAPHS COMPOSED OF K WHITE } z_1\text{-CIRCLES} \\ \text{LABELLED } 1, \dots, K \text{ RESPECTIVELY, SOME OR} \\ \text{NO BLACK } z_1\text{-CIRCLES AND SOME OR NO f-BONDS.} \end{array} \right. \quad (4.7)$$

E.g.  $u_2(1,2) = \bullet + \bullet + \bullet + \bullet + \dots$

If we now use the  $\rho_K - u_K$  relation (equation (2.14)), we find

$$\rho_K((1), \dots, (K)) = \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT SIMPLE GRAPHS CONSISTING} \\ \text{OF WHITE } z_1\text{-CIRCLES LABELLED } 1, \dots, K \text{ RESPECTIVELY,} \\ \text{SOME OR NO BLACK } z_1\text{-CIRCLES AND SOME OR NO f-BONDS} \\ \text{SUCH THAT THERE IS AT LEAST ONE PATH FROM EACH} \\ \text{BLACK CIRCLE TO A WHITE CIRCLE.} \end{array} \right. \quad (4.8)$$

e.g.  $\rho_1(1) = \text{diagram 1} + \text{diagram 2} + \text{diagram 3} + \dots$

$$\rho_2(1,2) = \text{diagram 1} + \text{diagram 2} + \text{diagram 3} + \text{diagram 4} + \text{diagram 5} + \text{diagram 6} + \dots$$

Every graph in (4.8) occurs in assorted forms with or without f-bonds between the white circles. We can thus replace groups of graphs by graphs with e-bonds between the white circles to obtain

$$\rho_K((1), \dots, (K)) = \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT CONNECTED SIMPLE GRAPHS} \\ \text{CONSISTING OF K WHITE } z_1\text{-CIRCLES LABELLED BY} \\ \text{1, \dots, K RESPECTIVELY, SOME OR NO BLACK } z_1\text{-CIRCLES,} \\ \text{SOME OR NO f-BONDS AND AN e-BOND BETWEEN EVERY} \\ \text{PAIR OF WHITE CIRCLES.} \end{array} \right. \quad (4.9)$$

The proof is most simply given by writing  $e = 1 + f$  for the bonds in (4.9) and then multiplying out. An example is

$$\rho_2(1,2) = \text{diagram 1} + \text{diagram 2} + \text{diagram 3} + \dots$$

with  $\sim$  representing an e-bond.

Note further than as  $z \rightarrow 0$ ,

$$\frac{\rho_M(\langle 1 \rangle, \dots, \langle M \rangle)}{z_1(\langle 1 \rangle), \dots, z_1(\langle M \rangle)} \rightarrow \prod_{(i,j) \in K_M} e(i,j) \quad (4.10)$$

where  $K_M$  is the complete graph of  $M$  circles.

## V. CONVERGENCE OF FUGACITY EXPANSIONS

In this section we show that the fugacity expansion derived in the previous section can have a finite radius of convergence in the fugacity plane. The proof is by graphical methods, and is due to Penrose<sup>[23]</sup>. There are other proofs by different methods<sup>[24,25]</sup>, but this one suits the lecture course. We start with the equations

$$\frac{P(z)}{kT} = \frac{1}{|\Omega|} \log \Xi ; \quad \rho = z \frac{\partial}{\partial z} \frac{P(z)}{kT}$$

and equation (4.6). We may write them in the form

$$\frac{P(z)}{kT} = \sum_{\ell=1}^{\infty} b_{\ell} z^{\ell} , \quad \rho = \sum_{\ell=1}^{\infty} \ell b_{\ell} z^{\ell} \quad (5.1)$$

$$\text{where } b_{\ell} = \frac{1}{\ell |\Omega|} \int_{\Omega} d(1) \dots \int_{\Omega} d(\ell) A_{\ell}((1), \dots, (\ell))$$

$$= \lim_{\Omega \rightarrow \infty} \frac{1}{|\Omega|} \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT CONNECTED SIMPLE GRAPHS} \\ \text{WITH } \ell \text{ BLACK 1-CIRCLES AND SOME OR NO f-BONDS,} \end{array} \right. \quad (5.2)$$

and thus

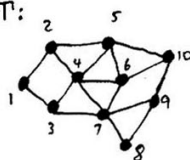
$$A_{\ell}((1), \dots, (\ell)) = \sum_{\Gamma} \prod_{(i,j) \in \Gamma} f(i,j) \quad (5.3)$$

SUM OVER ALL CONNECTED  
 GRAPHS WITH CIRCLES  
 LABELLED 1, ...,  $\ell$  .
 

 PRODUCT OVER ALL PAIRS OF  
 CIRCLES WITH BONDS BETWEEN  
 THEM IN THE GRAPH  $\Gamma$  .

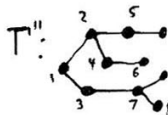
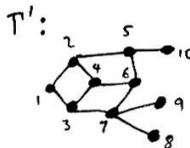
We now develop an estimate of the size of the  $A_{\ell}$ 's.

To each graph  $\Gamma$  we associate a unique Cayley tree  $\Gamma''$  in the following way. The graph  $\Gamma$  is labelled. To each circle  $i$  in  $\Gamma$  associate a weight  $w_i$  which is equal to the number of bonds in the shortest path from  $i$  to 1. Delete  $\Gamma$  from  $\Gamma$  all bonds joining circles of equal weight to get the graph  $\Gamma'$ . From each circle  $i \neq 1$  in  $\Gamma'$  there are one or more bonds to circles of weight  $w_i - 1$ .



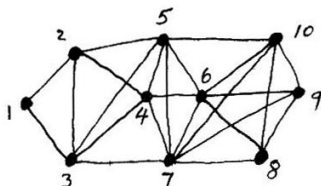
$w_1 = 0$   
 $w_2 = 1$   
 $w_3 = 1$   
 $w_4 = 2$   
 $w_5 = 2$   
 $w_6 = 3$   
 $w_7 = 2$   
 $w_8 = 3$   
 $w_9 = 3$   
 $w_{10} = 3$

Delete all these bonds except the one to the circle whose label is least. This gives the Cayley tree  $\Gamma''$ . From any Cayley tree  $T$  we may construct the set of graphs  $S(T)$  consisting of all graphs  $\Gamma$  with  $\Gamma'' = T$ .



The minimal graph in  $S(T)$  is  $T$  and the minimal graph is  $T^*$ , which is constructed  $(\Gamma'')^*$ :

as follows. Join all pairs of equal weight and then join every circle  $i \neq 1$  to all the circles whose weight is  $w_i - 1$  and whose label is greater than the label of the circle of weight  $w_i - 1$  to which  $i$  is already connected. Notice in our example that there is no 7-2 bond, nor a 10-4 bond. The number of graphs in  $S(T)$  is  $2^n$  where  $n$  is the number of bonds which are added to  $T$  to make  $T^*$ . We now write equation (5.3) as



$$A_{\ell} = \sum_{T \in \mathcal{T}} \left\{ \prod_{(i,j) \in T} f(i,j) \right\} \sum_{T \in \mathcal{S}(T)} \left\{ \prod_{(i,j) \in T-T} f(i,j) \right\}$$

SUM OVER LABELLED  
ℓ-CIRCLE TREES

so that

$$A_{\ell} = \sum_T \left\{ \prod_{(i,j) \in T} f(i,j) \right\} \prod_{(i,j) \in T^* - T} (1 + f(i,j)) \quad (5.4)$$

To proceed further we must specify the potential energy. We assume

$$\begin{aligned} \phi(r) &= +\infty & r < a \\ \phi(r) &\leq Ar^{-v-\epsilon} & r > a \end{aligned} \quad (5.5)$$

where  $v$  is the dimensionality of the system. It has been shown<sup>[26]</sup> that for these potentials there is a lower bound  $\phi$  on the energy per particle in any configuration. That is, there exists a  $\phi$  such that

$$\sum_{j=2}^n \phi(i,j) \geq -2\phi$$

so that

$$\prod_{j=2}^n (1 + f(i,j)) \leq q = e^{2\phi/kT} \quad (5.6)$$

for all  $n > 0$  for configurations without hard core overlap.

For each circle  $i$  in  $T$  we define the set of circles

$$S_i = \left\{ \begin{array}{l} \text{SET OF ALL CIRCLES SUCH THAT } (i,j) \in T^* - T \\ \text{AND EITHER } w_j = w_i + 1 \text{ OR } w_j = w_i \text{ AND } j \succ i. \end{array} \right. \quad (5.7)$$



$S_1$  is empty. Let  $M$  be the largest label on a circle with maximum weight. By (5.7),  $S_M$  is empty. Thus there are at most  $(\ell-2)$  non-empty sets of this type. The circles in  $S_i$  are joined by bonds of  $T^*-T$ , by (5.7). Thus, every circle of weight  $w_i + 1$  that is joined to  $i$  by a bond of  $T$  is joined by a bond of  $T^*-T$  to every circle of weight  $w_i$  and label greater than  $i$ . These bonds of  $T^*-T$  joining every pair of circles in  $S_i$  correspond to factors  $1 + f$  in the product in equation (5.4). The hard core condition implies that if this product is non zero, then the configuration is a non-overlapping one.

Hence

$$\prod_{(i,j) \in T^*-T} (1 + f(i,j)) \leq q^{\ell-2}$$

so that

$$|A_\ell| \leq q^{\ell-2} \sum_T \prod_{(i,j) \in T} |f(i,j)| \quad . \quad (5.8)$$

If we now define  $B = \int d^3 \underline{r} |f(\underline{r})|$  than we have

$$|b_\ell| \leq \frac{1}{\ell!} q^{\ell-2} \sum_T B^{\ell-1} \quad . \quad (5.9)$$

The single  $f$  integrals are the only ones needed for a Cayley tree. The number of labelled Cayley trees of  $\ell$  circles is  $g^{[27]} \ell^{\ell-2}$  so that we now have an estimate of the  $b_\ell$ 's :

$$|b_\ell| \leq (q\ell)^{\ell-2} B^{\ell-1} / \ell! \quad (5.10)$$

Cuachy's  $n^{\text{th}}$  root test then gives us a lower bound on the radius of convergence  $R$  of the series (5.1). We have

$$R \geq 1/\text{eq } B. \quad (5.11)$$

This means that at least for some potentials, the graphical expansions converge at small but finite fugacity.

For hard core systems we can find an upper bound on the radius of convergence. We can write

$$\Xi(z) = \prod_{\alpha=1}^M (1 - z/z_\alpha)$$

where  $M$  is the maximum number of hard spheres which will fit into the region  $\Omega$ , and  $\{z_\alpha\}_{\alpha=1}^M$  are the zeros of  $\Xi(z)$ , a finite polynomial.

However,

$$\frac{1}{|\Omega|} \log \Xi = \sum_{\ell=1}^{\infty} b_\ell z^\ell$$

so that

$$|\Omega| \ell b_\ell = - \sum_{\alpha} z_\alpha^{-\ell}.$$

Now, the radius of convergence must be closer to the origin than the nearest zero of the partition function so

$$| |\Omega| \ell b_\ell | \leq \sum_{\alpha} |z_\alpha|^{-\ell} \leq \frac{M}{R^\ell}.$$

Hence

$$R \leq R_\ell = \left( \frac{M}{|\Omega|^\ell b_\ell} \right)^{1/\ell} \quad \forall \ell \quad (5.12)$$

and a useable lower bound can be constructed using  $b_2$  with  $\ell = 2$ .

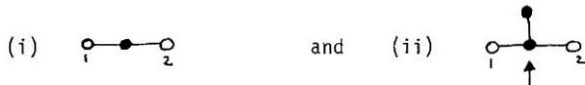
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25. D. Ruelle, *Ann. Phys. (N.Y.)* 25, 109 (1963).
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27. This is a classic result of graph theory first derived (we believe) by Polya. An excellent discussion of it is given in A.W. Ford and G.E. Uhlenbeck, "Studies in Statistical Mechanics". Eds. J. De Boer and G.E. Uhlenbeck. North Holland Publishing Co. Amsterdam (1960) Vol. I.

## VI. FIRST REPLACEMENT THEOREM

This is the second "topological reduction" theorem, the first having been the product theorem of section 3. This theorem is used to change the fugacity series of section 4 into density series, and the name is given it because it enables us to replace parts of the graphs in the fugacity series by  $\rho$ -circles. The other important feature of the theorem is its proof, since the method is used later in other topological reductions, especially the reductions used in modern perturbation theories.

We now define the concept of an ARTICULATION CIRCLE. A circle  $\alpha$  is an articulation circle if, upon its removal the component of which it is part separates into two or more pieces in such a way that at least one piece contains no white circles. The MULTIPLICITY of  $\alpha$  is the number of pieces into which the graph separates. A graph free of articulation circles is called 1-ineducible. Two examples might be



In (i), the black circle is not an articulation circle while in (ii) the arrowed black circle is an articulation circle of multiplicity 3.

We start with the h-correlation functions:

$$h_K(l, \dots, (K)) = u_K(l, \dots, (K)) / \rho_1(l) \dots \rho_1(K) \quad , \quad K \geq 2$$

and 
$$h_1(l) = \log[u_1(l) / z_1(l)] \quad ,$$

and we prove

$$h_K((1), \dots, (K)) = \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT CONNECTED SIMPLE} \\ \text{GRAPHS CONSISTING OF WHITE 1-CIRCLES} \\ \text{LABELLED } 1, \dots, K \text{ RESPECTIVELY, SOME OR} \\ \text{NO BLACK } z_1\text{-CIRCLES AND AT LEAST ONE f-BOND} \\ \text{SUCH THAT THE GRAPHS ARE FREE OF WHITE} \\ \text{ARTICULATION CIRCLES.} \end{array} \right. \quad (6.1)$$

To see how this theorem works, consider the graphical sum for  $h_K$  from equations (5.1) and (4.7). Attached to the  $K$  white circles will be graphs:



so that we can write the sum of a large number of graphs as

$$\left( \text{graph with circles 1, 2, 3} \right) * \left[ \text{graph with circle 3} + \text{graph with circle 1} + \text{graph with circle 3 and a black circle} + \text{graph with circle 3 and two black circles} + \text{graph with circle 3 and a black circle and a white circle} + \dots \right]$$

and the graphs in the square braces form the fugacity expansion for  $\rho_1(3)$ .

To prove (6.1) for  $K \geq 2$ , we write

$$u_K((1), \dots, (K)) = h_K((1), \dots, (K)) \rho_1(1) \dots \rho_1(K) \quad .$$

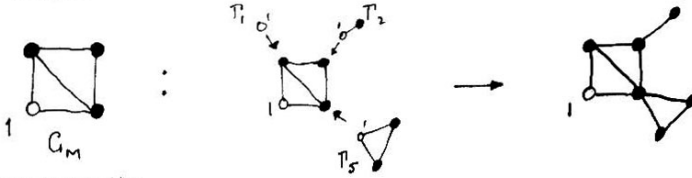
We substitute (6.1) for  $h_K$  and (4.8) for each  $\rho_1(i)$  and carry out the multiplication. The result is the expansion (4.7) for  $u_K$ , and (6.1) is proven. For  $K = 1$  the result follows by using the fugacity series for  $u_1(1)$  (equation (4.7)) and the product theorem.

A graph  $G$  in (6.1) contains a MAXIMAL 1-IRREDUCIBLE ROOTED SUBGRAPH,  $G_M$ . This is the maximal subgraph of  $G$  which contains all its white circles but no articulation circles. We can construct  $G$  from

$G_M$  by replacing each black-circle of  $G_M$  by a graph  $\Gamma_\alpha$  of the  $z_1$ -circle, f-bond expansion of  $\rho_1(1)$  :

$$\rho_1(1) = \frac{1}{\Gamma_1} + \frac{1}{\Gamma_2} + \frac{1}{\Gamma_3} + \frac{1}{\Gamma_4} + \frac{1}{\Gamma_5} + \dots \quad (6.2)$$

For example



We now prove the

FIRST REPLACEMENT THEOREM:

The sum of all graphs appearing in the  $h_K$  expansion in (6.1) that have the same  $G_M$  is equal in value to the graph  $\hat{G}_M$  which is  $G_M$  with  $\rho_1$ -circles instead of  $z_1$ -circles. (6.3)

To prove this theorem we first write (6.2) as

$$\rho_1(i) = \sum_{\alpha} \Gamma_{\alpha}(i) . \quad (6.4)$$

We may write  $\hat{G}_M = \frac{1}{\sigma_M} I_M$ , and the integrand in  $I_M$  contains the density.

We replace the density by (6.4) whenever it occurs. We write  $\Gamma_{\alpha}$  as  $I_{\alpha} / \sigma_{\alpha}$ , where  $\sigma_{\alpha}$  is the symmetry number of  $\Gamma_{\alpha}$ . The result is a product of sums of integrals. We can multiply out and get a single sum of integrals multiplied by factors. If  $G_M$  has  $M$  black circles, then a typical term in the sum is an integral  $I \times (\sigma_M \sigma_{\alpha_1} \dots \sigma_{\alpha_M})^{-1}$  where

the integrand is a product of  $f(i,j)$ 's and  $\mathbf{z}_1(i)$ 's. Every integral in this sum can be seen to occur in (6.1) and every integral associated with a graph in (6.1) occurs in our new sum. The only problem remaining is to ensure that the integrals in the new sum are counted the same way as in (6.1). A given term  $t$  in the new sum will correspond to a graph of (6.1) times a number not necessarily 1 because the symmetry number of the graph is not necessarily  $\sigma_M^{\sigma_{\alpha_1}} \dots \sigma_{\alpha_M}$ . In general there will be other terms in the sum which are indistinguishable from  $t$  in that they have the value  $I / \sigma_M^{\sigma_{\alpha_1}} \dots \sigma_{\alpha_M}$ , but black circles will have different dummy labellings. Let there be  $S$  such terms, including  $t$ . Their sum is then  $\frac{S}{\sigma_M^{\sigma_{\alpha_1}} \dots \sigma_{\alpha_M}}$ . For our theorem to hold we must now prove that the symmetry number  $\sigma_I$  of the graph  $G_I$  associated with  $I$  is  $\sigma_M^{\sigma_{\alpha_1}} \dots \sigma_{\alpha_M} / S$ .

Proof:

We calculate  $\sigma_I$  using a second labelling. We whiten all the black circles of  $G_M$  and label them  $K+1, \dots, K+M$ .  $S$  is then the number of distinguishable ways of labelling the circles  $K+1, \dots, K+M$  with labels  $\alpha_1, \dots, \alpha_M$  - i.e. the number of distinguishable ways of attaching the  $\Gamma_\alpha$  graphs to  $G_M$ . Note that  $\alpha_i$  and  $\alpha_j$  may be equal for  $i \neq j$  so that  $\Gamma_{\alpha_i}$  may be the same as  $\Gamma_{\alpha_j}$ . If they are all the same,  $S = 1$  and if they are all different  $S = M!$  We put

$$\sigma_I = \hat{\sigma} \sigma_{\alpha_1} \dots \sigma_{\alpha_M}$$



where  $\hat{\sigma}$  is the number of permutations among the  $\alpha_1, \dots, \alpha_M$  (or among the second set of labels  $K+1, \dots, K+M$ ) which leave the doubly labelled graph invariant. But the group of permutations among the labels  $\alpha_1, \dots, \alpha_M$  that leaves the doubly labelled graph invariant is a subgroup of the larger group of permutations which leave the singly labelled graph invariant. By Lagrange's theorem on the order of subgroups of finite groups, the ratio of the orders of the two groups is just the number of distinguishable ways that the double labelling can be done.

That is

$$S = \sigma_M / \hat{\sigma}$$

whence

$$\sigma_1 = \frac{\sigma_M^{\sigma_1} \dots \sigma_{\alpha_M}}{S}$$

and our result, and thus (6.3) is proven. From (6.3) and (6.1) we obtain

$$h_K((1), \dots, (K)) = \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT CONNECTED SIMPLE} \\ \text{GRAPHS WITH } K \text{ WHITE 1-CIRCLES LABELLED} \\ 1, \dots, K \text{ RESPECTIVELY, SOME OR NO BLACK} \\ \rho_1\text{-CIRCLES, AND AT LEAST ONE } f\text{-BOND SUCH} \\ \text{THAT THE GRAPHS ARE 1-IRREDUCIBLE} \end{array} \right. \quad (6.5)$$

for  $K \geq 2$  while for  $K = 1$  we obtain

$$h_1(1) = \log_{\rho_1}(1) - \log_z(1) = \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT CONNECTED} \\ \text{SIMPLE GRAPHS CONSISTING OF A WHITE} \\ \text{1-CIRCLE LABELLED 1, ONE OR MORE} \\ \text{BLACK } \rho_1\text{-CIRCLES AND } f\text{-BONDS SUCH} \\ \text{THAT THE GRAPHS ARE 1-IRREDUCIBLE.} \end{array} \right. \quad (6.6)$$

In the next section we proceed to use the first replacement theorem to develop density expansions of other interesting quantities.

## VII. DENSITY EXPANSIONS

Equation (2.14) gives us

$$\rho_K((1), \dots, (K)) = \sum \prod_{\alpha} u_{\alpha}(i_1, \dots, i_{n_{\alpha}}) \quad .$$

If we factor out the density functions attached to the white circles in this expression we find

$$g_K((1), \dots, (K)) = \sum \prod_{\alpha} h_{\alpha}(i_1, \dots, i_{n_{\alpha}}) \quad .$$

substituting for  $h_{\alpha}$  in this expression from (6.5) and (6.6) we find

$$g_K((1), \dots, (K)) = \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT SIMPLE GRAPHS CONSISTING} \\ \text{OF WHITE 1-CIRCLES LABELLED } 1, \dots, K \text{ RESPECTIVELY,} \\ \text{SOME OR NO BLACK } \rho_1\text{-CIRCLES AND SOME OR NO} \\ \text{f-BONDS SUCH THAT THERE IS A PATH FROM EACH} \\ \text{BLACK CIRCLE TO A WHITE CIRCLE AND THE GRAPHS} \\ \text{ARE 1-IRREDUCIBLE} \end{array} \right. \quad (7.1)$$

We can go a little further by the argument leading to (4.9) and insist that each graph contain a complete graph  $K_K$  of e-bonds:

$$g_K((1), \dots, (K)) = \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT AT-LEAST DOUBLY CONNECTED} \\ \text{SIMPLE GRAPHS CONSISTING OF } K \text{ WHITE 1-CIRCLES} \\ \text{LABELLED } 1, \dots, K \text{ RESPECTIVELY AND FORMING} \\ \text{A } K_K \text{ WITH e-BONDS, SOME OR NO BLACK } \rho_1\text{-CIRCLES} \\ \text{AND SOME OR NO f-BONDS.} \end{array} \right. \quad (7.2)$$

To develop a density expansion for  $\log \Xi$ , we note from (3.13)

that

$$\rho_1(1) = \frac{z_1(1)}{\Xi} \frac{\delta \Xi}{\delta z_1(1)}$$

or

$$\delta \log \Xi = \int d(1) \delta z_1(1) \rho_1(1) / z_1(1) - \int d(1) \log z_1(1) \delta \rho_1(1) \quad , \quad (7.3)$$

$$= \delta \int d(1) \rho_1(1) \log z_1(1) - \int d(1) \log z_1(1) \delta \rho_1(1) \quad . \quad (7.4)$$

Equation (6.6) now gives us

$$\begin{aligned} \delta \log \Xi = & \delta \int d(1) \rho_1(1) \log z_1(1) \\ & - \int d(1) \delta \rho_1(1) \left\{ \log \rho_1(1) - [\text{SUM OF GRAPHS ON RIGHT SIDE OF (6.6)}] \right\}. \end{aligned} \quad (7.5)$$

We now use the functional differentiation concept backwards to give

$$\log \Xi = \int d(1) \rho_1(1) \log z_1(1) - \int d(1) \rho_1(1) [\log \rho_1(1) - 1] + H(\rho_1, f) \quad (7.6)$$

apart from an additive constant independent of  $\rho$  which may be evaluated by using the ideal gas result. The term  $H(\rho_1, f)$  is given by

$$H(\rho_1, f) = \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT CONNECTED SIMPLE GRAPHS} \\ \text{COMPOSED OF BLACK } \rho_1\text{-CIRCLES, ONE OR MORE } f\text{-BONDS} \\ \text{AND 1-IRREDUCIBLE.} \end{array} \right. \quad (7.7)$$

This is usually called the Helmholtz free energy or excess Helmholtz free energy.

Since  $h_1(1) = \log \rho_1(1) - \log z_1(1)$  we have

$$\log \Xi = \int d(1) \rho_1(1) + H(\rho_1, f) - \int d(1) \rho_1(1) h_1(1) \quad . \quad (7.8)$$

For a uniform system this result reduces to

$$\frac{p|\Omega|}{kT} = \rho|\Omega| + |\Omega| \sum_k \frac{1}{k+1} \rho^{k+1} \beta_k - \sum_k \rho^{k+1} \beta_k \quad ,$$

or the well known virial expansion of the pressure

$$p/kT = \rho - \sum_k \frac{k}{k+1} \rho^{k+1} \beta_k \quad . \quad (7.9)$$

We now turn to the direct correlation function  $C(1,2)$  introduced in equations (2.24) and (2.25). The functional definition is

$$C(1,2) = \frac{\delta}{\delta \rho_1(2)} \log [\delta \log \Xi / \delta z_1(1)] \quad .$$

Since  $u_1(1)/z_1(1) = \delta \log \Xi / \delta z_1(1)$  ,  $\rho_1(1) = u_1(1)$  and

$h_1(1) = \log[\rho_1(1)/z_1(1)]$  ,  $C(1,2)$  may be written in the form

$$C(1,2) = \delta h_1(1) / \delta \rho_1(2) \quad (7.10)$$

To carry out this functional differentiation we use the graphical expansion (6.6) of  $h_1(1)$  and the result (3.5). Each graph in (6.6) contains only one white circle, so that it cannot be disconnected by the removal of any one circle. We call a circle a **CONNECTING CIRCLE** if its removal disconnects the component of which it is part. The graphs in (6.6) are free of connecting circles and remain so when one circle is whitened in the differentiation process. Thus

$$C(1,2) = \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT CONNECTED SIMPLE GRAPHS} \\ \text{CONSISTING OF TWO WHITE 1-CIRCLES LABELLED 1 AND 2} \\ \text{RESPECTIVELY, SOME OR NO BLACK } \rho_1\text{-CIRCLES AND f-BONDS} \\ \text{SUCH THAT THE GRAPHS ARE FREE OF CONNECTING CIRCLES.} \end{array} \right. \quad (7.11)$$



or

$$h_2(1,2) = c(1,2) + \int d(3) c(1,3) \rho_1(3) h_2(3,2) \quad . \quad (7.13)$$

This is the Ornstein Zernike equation, previously encountered as (2.24) and we have now proved the equivalence of the two definitions (2.24) and (2.25) of the direct correlation function  $c(1,2)$ .

We now develop some expansions of higher order distribution functions which are useful in studying the asymptotic properties of K-particle distribution functions. One such relation which is well known is the Kirkwood superposition approximation:  $g_3(1,2,3) \approx g_2(1,2)g_2(2,3)g_2(3,1)$ . We assume  $K > 1$  and define the POTENTIAL OF MEAN FORCE  $\psi_K((1), \dots, (K))$  as  $-kT \log g_K((1), \dots, (K))$ . We subtract the actual potential  $V_K$  and work with the quantity

$$w_K((1), \dots, (K)) = \log g_K((1), \dots, (K)) + \frac{1}{kT} V_K((1), \dots, (K)) \quad . \quad (7.14)$$

We can write  $w_K$  as a sum of a set of graphs with two white circles plus a sum of a set with three white circles etc. Hence

$$w_K((1), \dots, (K)) = \sum_{2 \leq S \leq K} \sum_{\{i_1, \dots, i_S\} \in \mathcal{N}} w_S(i_1, \dots, i_S) \quad (7.15)$$

where  $\mathcal{N}$  is the set of all S-tuples of the form  $\{i_1, \dots, i_S\}$  such that  $i_i < i_j$  for  $i < j$  and  $1 \leq i \leq K$ . We now use (7.2) to give a graphical sum for  $g_K((1), \dots, (K)) / \exp[-\frac{1}{kT} V_K((1), \dots, (K))]$  and then use the product theorem to find the logarithm of the sum. If we compare

the resulting expansion with (7.15) we find

$$\omega_K((1), \dots, (K)) = \text{THE SUM OF ALL DISTINCT CONNECTED SIMPLE GRAPHS CONSISTING OF } K \text{ WHITE 1-CIRCLES LABELLED BY } 1, \dots, K \text{ RESPECTIVELY, AT LEAST ONE BLACK } \rho_1\text{-CIRCLE AND } f\text{-BONDS SUCH THAT EACH GRAPH IS FREE OF ARTICULATION CIRCLES. ALSO, EACH PAIR OF BLACK CIRCLES IN A GRAPH IS CONNECTED BY AT LEAST ONE PATH THAT DOES NOT PASS THROUGH ANY WHITE CIRCLE AND THERE IS NO BOND BETWEEN ANY PAIR OF WHITE CIRCLES.}$$

(7.16)

By induction from (7.15) we can express  $\omega_K$  in terms of the  $w_K$  :

$$\omega_K((1), \dots, (K)) = \sum_{2 \leq S \leq K} \sum_{\{i_1, \dots, i_S\} \subset \mathcal{N}} (-1)^{S+K} w_S((i_1), \dots, (i_S)) .$$

(7.17)

We can take the exponential of (7.17),  $\exp(\omega_K)$  being calculated from (7.16) by using the product theorem. Interchanging the sides of the equation we find

$$\frac{g_K((1), \dots, (K))}{\prod_{S=2}^{K-1} \left\{ \sum_{\{i_1, \dots, i_S\} \subset \mathcal{N}} g_S((i_1), \dots, (i_S)) \right\}} (-1)^{S+K+1} = 1 + \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT} \\ \text{SIMPLE GRAPHS CONSISTING} \\ \text{OF } K \text{ WHITE 1-CIRCLES} \\ \text{LABELLED } 1, \dots, K \\ \text{RESPECTIVELY, AT LEAST ONE} \\ \text{BLACK } \rho_1\text{-CIRCLE AND } f\text{-BONDS SUCH THAT EVERY} \\ \text{GRAPH IS 1-IRREDUCIBLE, EVERY BLACK CIRCLE} \\ \text{IS CONNECTED TO EVERY WHITE CIRCLE BY AT} \\ \text{LEAST ONE PATH NOT PASSING THROUGH OTHER} \\ \text{WHITE CIRCLES AND NO BONDS JOINING ANY} \\ \text{PAIR OF WHITE CIRCLES.} \end{array} \right.$$

(7.18)



In this equation, the left hand side has  $g_K(1, \dots, K)$  with as accurate an approximation possible to  $g_K$  made from  $\{g_N\}_{N=1}^{K-1}$  factored out. We can, instead, factor out an approximation made solely from  $g_2$ . This yields

$$\frac{g_K(1, \dots, K)}{\prod_{1 \leq i < j \leq K} g_2(i, j)} = 1 + \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT SIMPLE GRAPHS} \\ \text{CONSISTING OF } K \text{ WHITE 1-CIRCLES LABELLED} \\ \text{1, \dots, K RESPECTIVELY, AT LEAST 1 BLACK} \\ \text{p}_1\text{-CIRCLE AND f-BONDS SUCH THAT EVERY GRAPH} \\ \text{IS FREE OF ARTICULATION CIRCLES, EVERY BLACK} \\ \text{CIRCLE IS CONNECTED TO AT LEAST 3 WHITE} \\ \text{CIRCLES BY A PATH USING NO INTERMEDIATE} \\ \text{WHITE CIRCLES, WHILE THERE IS NO BOND} \\ \text{JOINING ANY PAIR OF WHITE CIRCLES.} \end{array} \right. \quad (7.19)$$

Equations (7.18) and (7.19) are the same for  $K = 3$  and setting the sum of graphs equal to zero yields the Kirkwood superposition approximation. These equations give ways to improve the approximation in a consistent way and show two methods for generalizing the approximation for  $K > 3$ .

We note that  $g_K \rightarrow 1$  for  $r(i, j) \rightarrow \infty$  where  $1 \leq i < j \leq K$ . As all distances  $\rightarrow \infty$ , the left hand **Sides** of (7.18) and (7.19) both tend to 1, but the first one tends more rapidly. This suggests that setting the sums of graphs on the right hand sides equal to zero yields a better approximation from (7.18) than from (7.19). Further, if a single point  $r_\alpha$  is moved away from the others, the left and right sides of (7.18) tend to 1. This is not true for (7.19) if  $K > 3$  and shows again that (7.18) can yield a more accurate expansion of  $g_K$  than does (7.19).

# VIII. SECOND REPLACEMENT THEOREM

The techniques introduced in this section are not much used directly, but the theorem proved to use them is crucial in the development of perturbation theories. We now define an ARTICULATION PAIR OF CIRCLES. Two circles  $\gamma_1$  and  $\gamma_2$  constitute an articulation pair if, on their removal from a component of the graph, the component separates into two or more parts, one of which contains at least one circle but no white circle, another of which contains at least one circle. A graph free of articulation circles and articulation pairs is 2-IRREDUCIBLE. We now use this circle to affect a topological reduction of the graphs in equations (7.16), (7.18) and (7.19).

We consider a typical graph  $G$  from one of these expansions for  $n \geq 3$ , and call the maximal subgraph of  $G$  which is free of articulation circles and articulation pairs of circles and yet contains all the white circles of  $G$  the MAXIMAL 2-IRREDUCIBLE ROOTED SUBGRAPH of  $G$  and denote it by  $G_M$ . Every graph in these  $f$ -bond  $\rho_1$ -circle expansion has a unique  $G_M$ . We can construct  $G$  from  $G_M$  by replacing each bond of  $G_M$  with some graph of the  $f$ -bond  $\rho_1$ -circle expansion of  $h_2(1,2)$  (see equation (6.5)). A typical bond  $B$  in  $G_M$  touches two circles  $\gamma_1$  and  $\gamma_2$ , one at each end. We replace  $B$ ,  $\gamma_1$  and  $\gamma_2$  by a graph  $\Gamma_\alpha$  of the  $f$ -bond  $\rho_1$ -circle expansion of  $h_2(1,2)$ . The white circles of  $\Gamma_\alpha$  must be delabelled and blackened before one goes on  $\gamma_1$ , the other on  $\gamma_2$ .

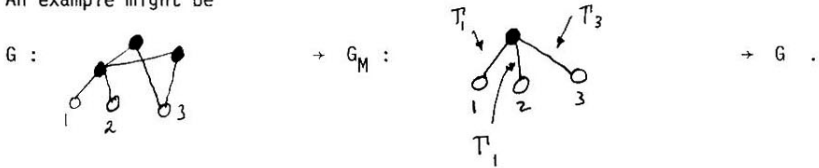
We write (6.5) in the form

$$h_2(1,2) = \sum_{\alpha} \Gamma_{\alpha}(1,2) \quad (8.1)$$

$$= \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} + \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} + \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} + \dots$$

$\Gamma_1 \quad \Gamma_2 \quad \Gamma_3$

An example might be



We now state and prove the

SECOND REPLACEMENT THEOREM.

The sum of all graphs appearing in (7.16), (7.18) or (7.19) that have the same  $G_M$  is equal in value to the graph  $\hat{G}_M$  obtained by letting all the bonds of  $G_M$  be  $h_2$  bonds. All black circles remain black circles and all white circles remain white circles. (8.2)

The proof proceeds in exactly the same way as for the first replacement theorem. We may write  $\hat{G}_M = \frac{1}{\sigma_M} I_M$ . The integrand in  $I_M$  contains  $h_2(1,2)$ . We replace  $h_2(1,2)$  wherever it appears by the expansion (8.1) and expand the resulting products so that  $\hat{G}_M$  is a sum of integrals multiplied by factors. If  $\hat{G}_M$  has  $M$  bonds, then a typical term  $t$  in the sum is an integral  $I \times (\sigma_M^{\sigma_{\alpha_1} \dots \sigma_{\alpha_M}})^{-1}$  where the integrand is a product of  $f(i,j)$ 's and  $z_1(j)$ 's. Each of these integrals occurs in the expansion we are considering, and each

integral in the expansion occurs in the sum. The only thing remaining is to ensure that the symmetry number  $\sigma$  of the graph in the expansion with the same integral as in the term  $t$  is given by

$$\sigma = \sigma_M^{\sigma_{\alpha_1}} \dots \sigma_{\alpha_M} / S \quad (8.3)$$

where  $S$  is the number of terms in the expansion from  $\hat{G}_M$  which are indistinguishable from  $t$ , except for different dummy labellings. The proof of (8.3) goes through in the same way if for the first replacement theorem. The only non-trivial change is the double labelling used. Each label in the second set of labels is attached to a bond of  $\hat{G}_M$  rather than a circle and it has a direction as well as an index. Typical labels can be  $\alpha(\rightarrow)$  or  $\alpha(\leftarrow)$ . If  $\alpha(\rightarrow)$  implies that the graph  $\Gamma_\alpha(i,j)$  is attached to the circles  $(i,j)$ , then  $\alpha(\leftarrow)$  implies that  $\Gamma_\alpha(j,i)$  is attached to  $(i,j)$ . The label  $\alpha(\rightarrow)$  is different from  $\alpha(\leftarrow)$  only if  $\Gamma_\alpha(i,j) \neq \Gamma_\alpha(j,i)$ . With these changes the proof of the second product theorem goes through without too much difficulty.

This theorem implies that for  $K \geq 3$ , equations (7.16), (7.18) and (7.19) can be changed by replacing  $f$ -bonds with  $h_2$ -bonds and insisting that each graph be free of articulation pairs. The result for (7.19) means that we can change (7.2) by insisting that the graphs be at least triply connected, and as well as changing the  $f$ -bonds to  $h_2$ -bonds, we change the  $e$ -bonds to  $g_2$ -bonds. Thus

$$g_K((1), \dots, (K)) = \text{THE SUM OF ALL DISTINCT AT LEAST TRIPLY} \\ \text{CONNECTED GRAPHS CONSISTING OF } K \text{ WHITE} \\ \rho_1\text{-CIRCLES FORMING A } K_K \text{ WITH } g_2\text{-BONDS AND} \\ \text{LABELLED } 1, \dots, K \text{ RESPECTIVELY, SOME OR NO} \\ \text{BLACK } \rho_1\text{-CIRCLES AND SOME OR NO } h_2\text{-BONDS.} \quad (8.4)$$

This completes our analysis of exact graphical expansions in classical statistical mechanics. In the remaining sections we shall apply the techniques developed above to the study of approximate methods.

## IX. GRAPHICAL DERIVATIONS OF STANDARD APPROXIMATIONS

In this section we discuss two approximate techniques for studying the graphical expansions derived in the previous sections. The two techniques are the Percus Yevick approximation (PY)<sup>[28]</sup> and the hypernetted chain approximation (HNC)<sup>[29,30]</sup>. We emphasize these two approximations because of their importance in liquid physics<sup>[31]</sup>. Both approximations work in the same way: a large class of graphs in the expansion for  $h_2(1,2)$  is summed in terms of  $h_2(1,2)$ ,  $C(1,2)$  and  $\phi_2(1,2)$  and an integral equation for  $h_2(1,2)$  and  $C(1,2)$  is developed. These can then be solved analytically<sup>[1-5,32,33]</sup>, numerically<sup>[9,10]</sup> or even approximately.

We start with the expansion for  $h_2(1,2)$  of equation (6.5):

$$h_2(1,2) = \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT CONNECTED SIMPLE GRAPHS} \\ \text{CONSISTING OF 2 WHITE 1-CIRCLES LABELLED 1,2} \\ \text{RESPECTIVELY, SOME OR NO BLACK } \rho_1\text{-CIRCLES AND AT} \\ \text{LEAST ONE f-BOND SUCH THAT THE GRAPHS ARE 1-IRREDUCIBLE.} \end{array} \right. \quad (9.1)$$

In section 7 we developed a similar expansion for  $C(1,2)$ .

$$C(1,2) = \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT SIMPLE GRAPHS CONSISTING} \\ \text{OF TWO WHITE 1-CIRCLES LABELLED 1,2 RESPECTIVELY,} \\ \text{SOME OR NO BLACK } \rho_1\text{-CIRCLES AND f-BONDS SUCH THAT} \\ \text{THE GRAPHS ARE 1-IRREDUCIBLE AND FREE OF NODAL CIRCLES.} \end{array} \right. \quad (9.2)$$

From the argument leading to equation (7.13) we can write

$$h_2(1,2) = C(1,2) + t(1,2) \quad (9.3)$$

so that  $t(1,2)$  must be defined by

$$t(1,2) = \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT SIMPLE GRAPHS CONSISTING OF} \\ \text{TWO WHITE 1-CIRCLES LABELLED 1,2 RESPECTIVELY, AT} \\ \text{LEAST ONE BLACK } \rho_1\text{-CIRCLE AND AT LEAST 2 f-BONDS} \\ \text{SUCH THAT THE GRAPHS ARE 1-IRREDUCIBLE AND CONTAIN} \\ \text{AT LEAST ONE NODAL CIRCLE.} \end{array} \right. \quad (9.4)$$

We are now able to develop the PERCUS-YEVICK approximation.

We divide equation (7.2) for  $g_2(1,2)$  by  $e^{-\phi_2(1,2)/kT}$  to find

$$g_2(1,2)e^{\phi_2(1,2)/kT} = 1 + \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT CONNECTED} \\ \text{1-IRREDUCIBLE SIMPLE GRAPHS WITH} \\ \text{TWO WHITE 1-CIRCLES LABELLED 1,2} \\ \text{RESPECTIVELY, AT LEAST ONE BLACK } \rho_1\text{-CIRCLE} \\ \text{AND f-BOND WITH NO BOND BETWEEN 1 AND 2.} \end{array} \right.$$

$$= 1 + t(1,2) + B(1,2) \quad (9.5)$$

All the  $t(1,2)$  graphs appear on the right hand side of (9.5) because by (9.4) any graph in  $t(1,2)$  has a nodal circle and hence no  $(1,2)$  bond. The sum of graphs written  $B(1,2)$  is given by

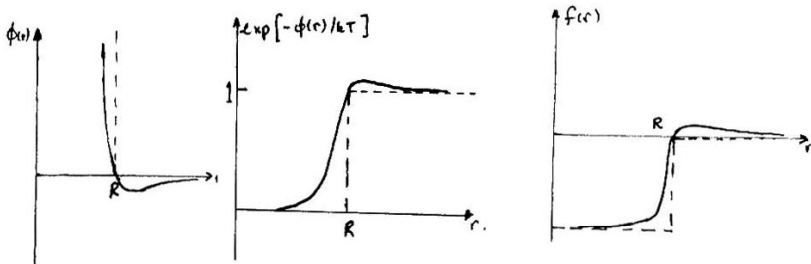
$$B(1,2) = \left\{ \begin{array}{l} \text{THE SUM OF ALL DISTINCT SIMPLE GRAPHS CONSISTING} \\ \text{OF TWO WHITE 1-CIRCLES LABELLED 1,2 RESPECTIVELY,} \\ \text{SOME BLACK } \rho_1\text{-CIRCLES AND f-BONDS AND WITH NO} \\ \text{ARTICULATION CIRCLES, NODAL CIRCLES OR (1,2) BONDS.} \end{array} \right. \quad (9.6)$$

$$= \begin{array}{c} \text{Diagram 1: Two white circles labeled 1 and 2, each connected to two black circles. The two black circles are connected to each other, forming a nodal circle.} \end{array} + \begin{array}{c} \text{Diagram 2: Two white circles labeled 1 and 2, each connected to two black circles. The two black circles are connected to each other, forming a nodal circle.} \end{array} + \dots = \begin{array}{c} \text{Diagram 3: Two white circles labeled 1 and 2, each connected to two black circles. The two black circles are connected to each other by a wavy line labeled 'e', representing an e-bond.} \end{array} + \dots$$



We have shown the first contributions to  $B(1,2)$ . The two leading order terms may be added together to form one term with an e-bond as shown. Since the symmetry number of both these graphs is 2 we have

$$\text{Diagram} = \frac{1}{2} \int d(3) \int d(4) f(1,3) f(2,3) f(1,4) f(2,4) \rho_1(3) \rho_1(4) \exp(-\phi_2(3,4)/kT)$$

It has become apparent that the Percus-Yevick approximation, which we'll introduce in a moment, is accurate for short-ranged highly repulsive interactions. Below we plot  $f(r)$  and  $\exp(-\phi(r)/kT)$  for short-ranged repulsive interactions and hard sphere interactions.



————— Real Potential      - - - - - Hard sphere potential

We see that when  $f(r)$  in the integrand of  is large,  $\exp[-\phi(r)/kT]$  is small, and when  $\exp[-\phi(r)/kT]$  is large,  $f(r)$  is small. Thus in the integrand, when the particles are close together,  $\exp[-\phi(r)/kT]$  is small and when they are far apart  $f(r)$  is small. Thus the integral is always fairly small. The two f-bond graphs making up  have nearly cancelled each other. Similar arguments



apply to the rest of the graphs in  $B(1,2)$  suggesting the

PERCUS YEVICK APPROXIMATION

$$B(1,2) = 0 \quad , \quad (9.7)$$

or, using (9.7) in (9.5) and then using (9.3) ,

$$C(1,2) = [1 + h_2(1,2)] [1 - e^{\phi_2(1,2)/kT}] \quad (9.8)$$

Equation (9.8) and the Ornstein-Zernike relation then form a soluble set of equations for  $h_2$  and  $C$  .

We now proceed to derive the hypernetted chain approximation.

We consider (7.14) for  $K = 2$  , which, by (7.16) may be written

$$\log g_2(1,2) + \frac{1}{kT} \phi_2(1,2) = W_2(1,2) = \Omega_2(1,2) \\ = \text{THE SUM OF ALL DISTINCT CONNECTED SIMPLE} \\ \text{GRAPHS CONSISTING OF 2 WHITE 1-CIRCLES} \\ \text{LABELLED 1,2 RESPECTIVELY, AT LEAST ONE} \\ \text{BLACK } \rho_1\text{-CIRCLE AND f-BONDS SUCH THAT EACH} \\ \text{GRAPH IS 1-IRREDUCIBLE, THERE IS NO f(1,2)} \\ \text{BOND AND EACH PAIR OF BLACK CIRCLES IS} \\ \text{CONNECTED BY AT LEAST ONE PATH WHICH DOES} \\ \text{NOT INCLUDE A WHITE CIRCLE.} \quad (9.9)$$

An examination of (9.4) shows that the right hand side of (9.9) contains  $t(1,2)$  (a sum of graphs with nodal circles) and other graphs. Hence

$$\log g_2(1,2) + \frac{1}{kT} \phi_2(1,2) = t(1,2) + E(1,2) \quad (9.10)$$





where  $E(1,2)$  is the sum of graphs on the right hand side of (9.9) which do not have nodal circles. We make the HYPERNETTED CHAIN APPROXIMATION:

$$E(1,2) = 0 \quad (9.11)$$

or, using (9.3) again and rearranging,

$$C(1,2) = h_2(1,2) - \frac{1}{kT} \phi_2(1,2) - \log(1+h_2(1,2)) \quad , \quad (9.12)$$

which again may be used in conjunction with the Ornstein-Zernike relation to obtain  $h_2$  and  $c$ .

To compare the two approximations, we note that a graph in  $E(1,2)$  is in  $B(1,2)$ , but not <sup>necessarily</sup> vice-versa, so that HNC counts more graphs than does PY, and should therefore be a better approximation. This is true for some systems with long range interactions<sup>[34]</sup>. However, for systems with only short-range repulsions, the PY approximation is better than the HNC approximation<sup>[35]</sup>. This is apparently because PY ignores two classes of graphs which approximately cancel each other (as seen in the analysis of ) while HNC sums part of one of these classes and hence misses the cancellation. For example  $E(1,2)$  includes , but not  and hence misses the approximate cancellation in  due to the e-bond. We might note that it is possible to extend these approximations by summing another class of diagrams not summed in either approximation<sup>[86]</sup>. Experience has shown, however that these new approximations, the PYII and HNC II are not really worth the extraordinary effort needed to use them<sup>[37]</sup>.

For comparison we outline the derivation of these approximations by functional differentiation. We start with the relation (7.10)

$$C(1,2) = \delta h_1(1) / \delta \rho_1(2) \quad (9.13)$$

from which we deduce

$$\delta \exp[h_1(1)] = \exp[h_1(1)] \int d(2) \delta \rho_1(2) C(1,2) + O((\delta \rho_1)^2) \quad (9.14)$$

Percus<sup>[38]</sup> suggested that  $\exp[h_1(1)]$  should be almost linear in density so that the first order term in  $\delta \rho_1$  in (9.14) should be sufficient, and chose as the perturbation producing the changes.

$$\delta \log z_1(i) = - \frac{1}{kT} \phi_2(0,i) \quad (9.15)$$

that is, he considered the effect of introducing another particle, labelled 0 into the system. We have for the new density function

$\rho_1^*(i)$ :

$$\rho_1^*(i) = \rho_2(0,i) / \rho_1(0) = \rho_1(i) g_2(0,i) \quad .$$

For the new  $h_1(i)$  we then have

$$\exp[h_1^*(i)] = \rho_1(i) g_2(0,i) / z_1(i) e^{-\phi_2(0,i)/kT} = \exp[h_1(i)] g_2(0,i) e^{\phi_2(0,i)/k}$$

Hence

$$\delta \rho_1(i) = \rho_1^*(i) - \rho_1(i) = \rho_1(i) h_2(0,i)$$

while

$$\delta \exp[h_1(i)] = \frac{\exp[h_1^*(i)] - \exp[h_1(i)]}{\exp[h_1(i)]} = \exp[h_1(i)] [g_2(0,i) e^{\phi_2(0,i)/kT} - 1] \quad .$$

Inserting these results in (9.14) and ignoring the  $(\delta \rho_1)^2$  terms we find

$$\begin{aligned} g_2(0,1)e^{\phi_2(0,1)/kT} - 1 &= \int d(2)\rho_1(2)h_2(0,2)c(1,2) \\ &= h_2(0,1) - c(0,1) \end{aligned}$$

by the Ornstein-Zernike equation. Rearranging, we get the PY equation (9.8). We can derive the HNC approximation in the same way by assuming  $h_1(1)$  rather than  $\exp[h_1(1)]$  is linear in  $\delta\rho_1$ .

From (9.13) we have

$$\delta h_1(1) = \int d(2)\delta\rho_1(2)c(1,2) + O((\delta\rho_1)^2) \quad (9.16)$$

and we can also write

$$\begin{aligned} h_1^*(i) &= \log [\rho_1(i)g_2(0,i)/z_1(i)e^{-\phi_2(0,i)}] \\ &= h_1(i) + \log g_2(0,i) + \phi_2(0,i)/kT \quad . \end{aligned}$$

Thus we have, using the earlier estimate for  $\delta\rho_1(2)$ ,

$$\begin{aligned} \log g_2(0,1) + \phi_2(0,1)/kT \\ &= \int d(2)\rho_1(2)h_2(0,2)c(1,2) \\ &= h_2(0,1) - c(0,1) \end{aligned}$$

by the Ornstein-Zernike relation. Rearrangement of this result gives

$$c(0,1) = h_2(0,1) - \frac{1}{kT} \phi_2(0,1) - \log(1 + h_2(0,1)) \quad ,$$

the HNC approximation of (9.12).

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## IONIC SYSTEMS

In this section we discuss how to adapt the graphical theory developed in the previous sections to handle systems with ionic interactions. Certain divergences in the theory are removed by recourse to the overall electrical neutrality of the system. We note that for dipolar systems the divergences are not quite so severe, but their handling is very much more complicated<sup>[39]</sup>, since they appear in spite of the electrical neutrality of the system and give rise to shape dependent effects. In this section we use the method of Friedman<sup>[40]</sup> to derive the Debye-Huckel free energy of a neutral ionic system.

We study a simple system of positive charges inversed in a uniform neutralizing background. The second virial coefficient for this potential then diverges and the upper bound  $R_2$  (from equation (5.12)) on the radius of convergence of the fugacity expansion is then zero. It is clearly necessary to do something, since power series in fugacity or density do not have any meaning at any finite values of  $z$  or  $\rho$ .

We begin by examining  $G$ , the excess free energy density over the ideal gas free energy density which may be written in the form

$$G = \sum_{n=2}^{\infty} \beta_n \rho^n \quad (10.1)$$

The two particle potential is  $\phi(1,2) = q^2/r(1,2)$ . If we examine

$$2B_2 = \lim_{R \rightarrow \infty} \int_0^R 4\pi r^2 (e^{-q^2/rkT} - 1) dr$$

by putting  $\lambda = 4\pi q^2/kT$  we find

$$2B_2 = \sum_{n=1}^{\infty} \frac{(-\lambda)^n}{n!} \lim_{R \rightarrow \infty} \int_0^R (4\pi r)^{1-n} dr .$$

For  $n \leq 4$ , these limits diverge as  $R \rightarrow \infty$ , while they diverge for  $n \geq 3$  near  $r = 0$ . The divergences at zero are artificial since the original form containing the exponential does not diverge at  $r = 0$  and further, there is usually a strongly repulsive core to handle it. The divergence as  $R \rightarrow \infty$  is real, however, and a similar divergence occurs in all the coefficients  $\beta_M$ . If we consider a finite system and then add up all the divergent parts, then take the infinite system limit, we may expect a convergent result, in accord with physics. To carry out this program, we introduce the k-bond:

$$k(i,j) = 1/r(i,j) \quad (10.2)$$

so that

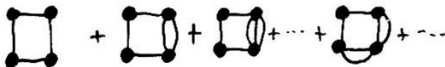
$$f(i,j) = \sum_{n=1}^{\infty} \left( -\frac{\lambda}{4\pi} \right)^n \cdot \frac{1}{n!} [k(i,j)]^n .$$

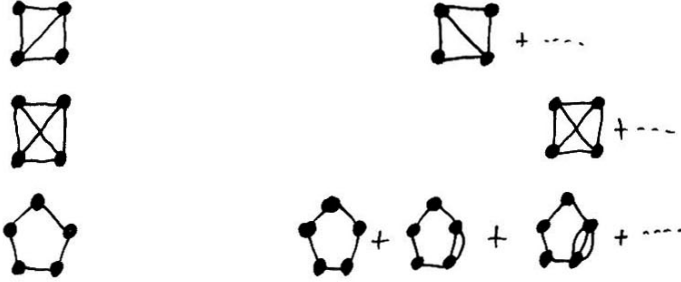
If we now compare the f-bond graphs for  $G$  with the resulting k-bond graphs, we find

f-bond graphs



k-bond graphs





The divergences which worry us are at large  $r$  in the integrands. Thus the most divergent terms of the M-circle graphs are those with fewest bonds. We add up the most divergent graphs for each  $M$  to get a first approximation for the free energy. We note that the  $\bullet\text{---}\bullet$  graph gives zero by the charge neutrality managed by the uniform neutralizing background. The most divergent graphs are the M-BOND polygons. We have

$$G_0 = \sum_{m=2}^{\infty} \frac{(-\rho\lambda)^M}{M!} \frac{(M-1)!}{2} \int dr_{12} \int dr_{13} \dots \int dr_{1n} k(1,2)k(2,3) \dots k(n-1,n)k(n,1) \quad (10.3)$$

where we have used the facts that the symmetry number of an  $M$  side polygon is  $2M$  and a factor  $M!$  in the numerator accounts for all the ways of labelling the graphs. We define  $\kappa^2 = \lambda\rho$  and let

$$p(r_{1,n+1}) = \int k(1,2)k(2,3) \dots k(n,n+1) dr_{12} \dots dr_{1n}$$

and introduce

$$q(r) = \sum_{n=1}^{\infty} (-\kappa^2)^{n-1} p_n(r) \quad (10.4)$$

From (10.3) and (10.4) we see that

$$G_D = \int_0^{\kappa} \kappa d\kappa \lim_{r \rightarrow 0} [k(r) - q(r)] \quad (10.5)$$



If we now take the Fourier transform of (10.4) we find

$$\hat{q}(t) = \int q(r) e^{i\mathbf{r} \cdot \mathbf{t}} d\mathbf{r} = \sum_{n=1}^{\infty} (-\kappa^2)^{n-1} [\hat{k}(t)]^n$$

by using the convolution nature of  $p(r)$ . The Fourier transform of  $k(r)$  is

$$\hat{k}(t) = 1/t^2$$

so that

$$\hat{q}(t) = -\kappa^{-2} \sum_{n=1}^{\infty} (-\kappa^2/t^2)^n = \frac{1}{\kappa^2 + t^2}.$$

Thus

$$q(r) = \frac{1}{(2\pi)^3} \int d\mathbf{t} \hat{q}(t) e^{-i\mathbf{r} \cdot \mathbf{t}} = e^{-\kappa r}/4\pi r \quad (10.6)$$

and equation (10.5) gives us

$$G_D = \kappa^3/12\pi \quad (10.7)$$

This result is proportional to  $\rho^{3/2}$  and hence non-analytic in  $\rho$  at  $\rho = 0$ . It is the well known Debye-Huckel expression for the excess free energy of a dilute electrolyte, with  $\kappa$  being the inverse Debye length for the electrolyte.

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## XI PERTURBATION THEORIES I: DEFINITIONS AND TECHNIQUES.

In the last two sections of these lectures we shall discuss the graph theoretical approach to thermodynamic perturbation theories. These theories are at present one of the main theoretical routes to the equilibrium properties of real and complex model systems and, so are of considerable importance in modern theories of dense fluids. In this section we introduce a variety of concepts which may be used in perturbation theories and in the next section we use them in an example.

The first thing we must examine is the interparticle potential  $\phi_2(1,2)$ . We consider systems of several species of particles. The only important difference that this makes to the preceding theory is that an integration of the form  $\int d(i)$  must now be taken to include a summation over particle species as well, the other modifications are all obvious. We write the two particle potential between  $\alpha$  and  $\beta$  in the form

$$\phi_{\alpha,\beta}(1,2) = \phi_{D\alpha\beta}(1,2) + v_{\alpha,\beta}(1,2) \quad (11.1)$$

where  $\phi_{D\alpha\beta}(1,2)$  is chosen so that the properties of a system with just that potential are well known and  $v_{\alpha,\beta}(1,2)$  is small. Of course, it may not be possible to satisfy both these requirements at once, and usually we are forced to make compromises over one or the other or both.

The potential determines the  $f(1,2)$  bond, and for these potentials there are two ways of writing the  $f$ -bond. We have

$$f_{\alpha,\beta}(1,2) = \exp[-\phi_{\alpha,\beta}(1,2)/kT] - 1 .$$

If we define

$$\psi_{\alpha,\beta}(1,2) = -\frac{1}{kT} v_{\alpha,\beta}(1,2) \quad (11.2)$$

then we may write

$$f_{\alpha,\beta}(1,2) = f_{D\alpha,\beta}(1,2) + [1 + f_{D\alpha,\beta}(1,2)] \sum_{n=1}^{\infty} \frac{1}{n!} [\psi_{\alpha,\beta}(1,2)]^n \quad (11.3)$$

where

$$f_{D\alpha,\beta}(1,2) = \exp[-\phi_{D\alpha,\beta}(1,2)/kT] - 1. \quad (11.4)$$

Using equation (11.3) we may replace graphical expansions with simple graphs with  $f$  bonds by composite graphs, between any two circles of which we may have no or one  $f_D$ -bonds and any number (including zero) of  $\psi$ -bonds. If  $\psi_{\alpha,\beta}(1,2)$  is small we may expect that only graphs with a small number of  $\psi$ -bonds contribute to the properties of the systems discussed. This break up of the  $f$ -bond into a perturbation part (the  $\psi$ -bonds) and a reference part (the  $f_D$ -bonds) appears to be particular useful when the perturbation part is long-ranged. The most well known treatments of such systems are those of Lebowitz, Stell and Baer<sup>[41]</sup> and of Andersen, Chandler and co-workers<sup>[42]</sup>. An often used reference pair potential <sup>is the hard sphere potential</sup>  $\phi$ , since we have good analytical approximations for its properties via the Percus-Yevick approximation<sup>[43]</sup> and even better numerical data via simulation techniques<sup>[44,45]</sup>.

An alternative way to split the  $f$ -bond might be to write

$$f_{\alpha,\beta}(1,2) = f_{D\alpha,\beta}(1,2) + F_{\alpha\beta}(1,2) \quad (11.5)$$

with

$$\begin{aligned} F_{\alpha\beta}(1,2) &= \exp[-\phi_{D\alpha\beta}(1,2)/kT] \{ \exp[\psi_{\alpha\beta}(1,2)] - 1 \} , \\ &= f_{\alpha\beta}(1,2) - f_{D\alpha\beta}(1,2). \end{aligned} \quad (11.6)$$

This division of the  $f$ -bond will give graphs with no or one  $f_D$ -bonds and no or one  $F$ -bonds but never one  $f_D$ -bond and one  $F$ -bond between any pair of circles in the graph. It would appear appropriate for systems in which the perturbation potential is repulsive and short-ranged, but has not been used as frequently as has (11.3).

We might note that the perturbation theories we develop are based on graphs with  $p$ -circles. However, there is very little understanding at present of the convergence properties of these expansions. A basic problem is that while the reference system may be in a one phase state, it is entirely possible for the perturbed system to be in a two phase state. The perturbation theory attempts to act at constant density, but this may not reflect physical reality. A recent attempt to modify this situation is that of Kumar and Penrose<sup>[46]</sup> who devised a constant fugacity expansion. They managed to write down the most general terms in their perturbation expansion, but have not yet been able to find any convergence properties of the series.

We have now introduced the ideas of reference and perturbation potentials, reference and perturbation bonds and composite graphs made up of such bonds with black and white circles. In the context of such composite graphs we introduce the idea of a REFERENCE ARTICULATION PAIR OF CIRCLES. This is a pair of circles whose removal from a component of a composite graph leaves the component in disconnected pieces, one of

which pieces has only reference bonds, at least one black circle and no white circles.

If we draw an  $f_D$  bond as ... and a  $\psi$  bond as \_\_\_\_ then some composite graphs might be

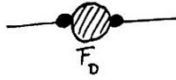


The pairs of circles marked with asterisks are reference articulation pairs. The object of this definition is, of course, to exclude such pairs from the graphs of a graphical expansion by replacing them with an  $h_{D\alpha\beta}(1,2)$ -bond, whose structure is assumed known along with the rest of the properties of the reference system. That this replacement is possible is a consequence of the second replacement theorem of action 8. The new graphical expansions will thus contain only  $h_D$ -bonds and  $\psi$ -bonds and no reference articulation pairs of circles.

The final idea which we want to introduce is that of the HYPERCIRCLE. It often occurs that we get parts of a graph being either of the form

$$(i) \quad \text{---} \bullet \text{---} \text{---} \bullet \text{---} \quad \text{OR} \quad (ii) \quad \text{---} \bullet \text{---} \quad . \quad (11.7)$$

We can add the two possibilities together as



(11.8)

where  $F_D$  is a hypercircle and

$$F_{D\alpha\beta}(1,2) = P_\alpha P_\beta h_{D\alpha\beta}(1,2) + P_\alpha \delta_{\alpha\beta} \delta(1,2) \quad . \quad (11.9)$$

Integration over the circle coordinate (2) in the delta function will reproduce graph (ii) in (11.7). It is usually the Fourier transform of  $F_D$  which is of interest and the Fourier transform of a delta function is particularly simple. The point of this new concept is to simplify the structure of some of the graphs which are added up in perturbation theories. The hypercircle in (11.9) has two circles on it. We point out that Lebowitz, Stell and Baer<sup>[41]</sup> introduced hypercircles with  $k$ -circles on them, which were related to sums of products of  $h_{D,k}$ ,  $h_{D,k-1}, \dots, h_{D,2}$  and delta functions. This enabled them to sum larger pieces of graphs than (11.9) will allow us to. However, since we at best know the two-particle distribution functions for the reference system, we shall restrict our attention to the simpler hypercircles of equation (11.9). We now go on to discuss an example of a perturbation theory to show how the ideas introduced in this section may be used.

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## XII PERTURBATION THEORIES II : EXAMPLE

The perturbation theory of Andersen and Chandler<sup>[47]</sup> is developed for a hard sphere reference potential. That is, we can write

$$\phi_{\alpha\beta}(1,2) = \begin{cases} \infty & r(1,2) < R_{\alpha\beta} \\ v_{\alpha\beta}(1,2) & r(1,2) > R_{\alpha\beta} \end{cases} \quad (12.1)$$

and

$$\phi_{D\alpha,\beta}(1,2) = \begin{cases} \infty & r(1,2) < R_{\alpha\beta} \\ 0 & r(1,2) > R_{\alpha\beta} \end{cases} \quad (12.2)$$

so that

$$\phi_{\alpha\beta}(1,2) = \phi_{D\alpha\beta}(1,2) + v_{\alpha\beta}(1,2) \quad (12.3)$$

We should notice that  $v_{\alpha\beta}(1,2)$  is undefined for  $r(1,2) < R_{\alpha\beta}$ . The perturbation theory takes advantage of this later, by assigning values to  $v_{\alpha\beta}(1,2)$  for  $r(1,2) < R_{\alpha\beta}$  which improve the accuracy of the approximation developed. From equations (12.1) and (12.2) we find the f-bond function for the full and reference potentials to be

$$f_{\alpha\beta}(1,2) = \exp\left[-\frac{1}{kT} \phi_{\alpha\beta}(1,2)\right] - 1 = \begin{cases} -1 & r(1,2) < R_{\alpha\beta} \\ \exp[-v_{\alpha\beta}(1,2)/kT] - 1 & r(1,2) > R_{\alpha\beta} \end{cases} \quad (12.4)$$

and

$$f_{D_{\alpha\beta}}(1,2) = \begin{cases} -1 & r(1,2) < R_{\alpha\beta} \\ 0 & r(1,2) > R_{\alpha\beta} \end{cases} \quad (12.5)$$

while

$$\psi_{\alpha\beta}(1,2) = -\frac{1}{kT} v_{\alpha\beta}(1,2) \quad (12.6)$$

We may write the excess Helmholtz free energy in the form

$$\frac{-Q}{|\Omega|kT} = \mathcal{A} = \frac{1}{|\Omega|} \left\{ \begin{array}{l} \text{THE SUM OF ALL CONNECTED 1-IRREDUCIBLE SIMPLE} \\ \text{GRAPHS WITH NO WHITE CIRCLES, TWO OR MORE} \\ \text{BLACK } \rho_1\text{-CIRCLES AND } f\text{-BONDS} \end{array} \right. \quad (12.7)$$

The two particle distribution functions have the expansion

$$\rho_{\alpha} \rho_{\beta} [g_{2\alpha\beta}(1,2) - 1] = \rho_{\alpha} \rho_{\beta} h_{2\alpha\beta}(1,2) = \left\{ \begin{array}{l} \text{THE SUM OF ALL CONNECTED SIMPLE GRAPHS} \\ \text{WITH TWO WHITE } \rho_1\text{-CIRCLES (ONE } \alpha \\ \text{SPECIES LABELLED 1, ONE } \beta \text{ SPECIES} \\ \text{LABELLED 2) SOME OR NO BLACK } \rho_1\text{-CIRCLES,} \\ \text{f-BONDS AND 1-IRREDUCIBLE.} \end{array} \right. \quad (12.8)$$

We now make the perturbation expansion of  $f$  splitting it into a reference part plus powers of the perturbation potential  $\psi$  (see equation 11.3)

and then find

$$\mathcal{A} = \frac{1}{|\Omega|} \left\{ \begin{array}{l} \text{THE SUM OF ALL MORE THAN SINGLY CONNECTED GRAPHS} \\ \text{WITH NO WHITE CIRCLES, 2 OR MORE BLACK } \rho_1\text{-CIRCLES,} \\ \text{AT MOST ONE } f_D\text{-BOND AND ANY NUMBER OF } \psi\text{-BONDS} \\ \text{BETWEEN ANY PAIR OF CIRCLES,} \end{array} \right. \quad (12.9)$$

while

$$\rho_{\alpha}\rho_{\beta}h_{2\alpha\beta}(1,2) = \left\{ \begin{array}{l} \text{THE SUM OF ALL CONNECTED GRAPHS WITH TWO WHITE} \\ \rho_1\text{-CIRCLES, (ONE } \alpha \text{ SPECIES LABELLED 1, ONE} \\ \beta \text{ SPECIES LABELLED 2) ANY NUMBER OF BLACK} \\ \rho_1\text{-CIRCLES, AT MOST ONE } f_D\text{-BOND AND ANY NUMBER} \\ \text{OF } \psi\text{-BONDS BETWEEN ANY PAIR OF CIRCLES.} \end{array} \right. \quad (12.10)$$



We are now able to develop our perturbation theory. If we consider (12.9) we see that there is a class of graphs with no  $\psi$ -BONDS. The sum of this class of graphs is the excess Helmholtz free energy for the reference system,  $\mathcal{A}_D$ . The other graphs all have at least one  $\psi$ -bond. If we replace this sum of graphs by a sum over graphs free of reference articulation pairs of circles and having  $h_D$ -bonds rather than  $f_D$  bonds, we get the same result. This can be seen by taking this new sum and inserting expansion (6.5) with  $K = 2$  for each  $h_D$ . All the terms in the result occur in (12.9) and vice-versa, and by appeal to the second replacement theorem of section 8, we see that we get the terms counted correctly. Thus we have

$$\mathcal{A} = \mathcal{A}_D + \frac{1}{|\Omega|} \left\{ \begin{array}{l} \text{THE SUM OF ALL MORE THAN SINGLY CONNECTED GRAPHS} \\ \text{WITH NO WHITE CIRCLES, TWO OR MORE BLACK } \rho_1\text{-CIRCLES,} \\ \text{AT MOST ONE } h_D\text{-BOND AND ANY NUMBER OF } \psi\text{-BONDS} \\ \text{CONNECTING ANY PAIR OF CIRCLES, AT LEAST ONE} \\ \psi\text{-BOND AND NO REFERENCE ARTICULATION PAIRS OF} \\ \text{CIRCLES.} \end{array} \right. \quad (12.11)$$

while

$$\rho_{\alpha}\rho_{\beta}h_{2\alpha\beta}(1,2) = \rho_{\alpha}\rho_{\beta}h_{D\alpha\beta}(1,2)$$

$$+ \left\{ \begin{array}{l} \text{THE SUM OF ALL CONNECTED GRAPHS WITH TWO WHITE } \rho_1\text{-CIRCLES} \\ \text{(ONE SPECIES } \alpha \text{ LABELLED 1 AND ONE SPECIES } \beta \text{ LABELLED} \\ \text{2) ANY NUMBER OF BLACK } \rho_1\text{-CIRCLES, AT MOST ONE } h_D\text{-BOND} \\ \text{AND ANY NUMBER OF } \psi\text{-BONDS CONNECTING ANY PAIR OF CIRCLES,} \\ \text{AT LEAST ONE } \psi\text{-BOND AND NO REFERENCE ARTICULATION PAIRS} \\ \text{OF CIRCLES.} \end{array} \right. \quad (12.12)$$

We can now add up parts of the graphical series in (12.11) and (12.12). First, we add up those graphs in (12.11) with but one  $\psi$ -bond. Since, by (12.6)  $\psi \rightarrow 0$  as  $T \rightarrow \infty$ , this sum is a good approximation to the total at high temperature. We call the result the High Temperature Approximation. In the rest of this section we represent a  $\psi$ -bond by  and an  $h_D$  bond by . There are only two graphs in  $\Omega_k$  with only one  $\psi$ -bond so that

$$|\Omega_k|_{\text{HTA}} = \text{---} + \text{---} \quad (12.13)$$

Any decoration of these graphs with more circles and  $h_D$ -bonds is in fact just writing down a part of the  $h_D$ -bond. That is, for example in



, the two circles at either end of the  $\psi$ -bond form a reference articulation pair. Hence since

$$g_{D\alpha\beta}(1,2) = 1 + h_{D\alpha\beta}(1,2), \text{ we have}$$

$$\begin{aligned}
 |\Omega| \mathcal{A}_{\text{HTA}} &= \frac{1}{2} \sum_{\alpha, \beta} \rho_{\alpha} \rho_{\beta} \int d(1) \int d(2) g_{D_{\alpha\beta}}(1,2) \psi_{\beta\alpha}(1,2) \\
 &= \frac{1}{2} |\Omega| \sum_{\alpha, \beta} \rho_{\alpha} \rho_{\beta} \int dr g_{D_{\alpha\beta}}(r) \psi_{\beta\alpha}(r). \quad (12.14)
 \end{aligned}$$

The approximation  $\mathcal{A} = \mathcal{A}_D + \mathcal{A}_{\text{HTA}}$  gives  $\mathcal{A}$  correct to  $O(T^{-1})$ .

To go further in adding up the perturbation graphs of equations (12.11) and (12.12), we must introduce the idea of a hyper circle and a "renormalized" potential. We define the RENORMALIZED POTENTIAL as

$$\rho_{\alpha} \rho_{\beta} D_{\alpha\beta}(1,2) = \left\{ \begin{array}{l} \text{THE SUM OF ALL CHAINS OF ONE OR MORE } \psi\text{-BONDS} \\ \text{CONNECTING TWO WHITE } \rho_1\text{-CIRCLES (ONE SPECIES} \\ \alpha \text{ LABELLED 1, ONE SPECIES } \beta \text{ LABELLED 2)} \\ \text{TOGETHER WITH THE RESULTS OF ALL POSSIBLE WAYS} \\ \text{OF INSERTING SEPARATE } h_D\text{-BONDS AT THE END OR} \\ \text{IN THE MIDDLE OF THE CHAIN.} \end{array} \right. \quad (12.15)$$

We note that for the potentials being discussed  $D_{\alpha\beta}(1,2)$  is a function only of the distance  $r(1,2)$ . Also, we can write

$$\rho_{\alpha} \rho_{\beta} D_{\alpha\beta}(r) = \rho_{\alpha} \rho_{\beta} \sum_{n=1}^{\infty} D_{\alpha\beta}^{(n)}(r) \quad (12.16)$$

where  $D_{\alpha\beta}^{(n)}(r)$  is the sum of all the chains in (12.15) with exactly  $n$   $\psi$ -bonds. Since we are using this idea to add up parts of the graphs in (12.11) and (12.13) we do not allow the chains to have any reference articulation pairs of circles. This means that the graphs do not have any  $h_D$ -bonds laid end to end. We call these objects "generalized chains".

Thus we have

$$\rho_\alpha \rho_\beta D_{\alpha\beta}^{(1)}(r) = \begin{array}{c} \text{---} \text{---} \\ \text{1} \quad \text{2} \end{array} + \begin{array}{c} \text{---} \text{---} \text{---} \\ \text{1} \quad \text{---} \quad \text{2} \end{array} + \begin{array}{c} \text{---} \text{---} \text{---} \\ \text{1} \quad \text{---} \quad \text{2} \end{array} + \begin{array}{c} \text{---} \text{---} \text{---} \text{---} \\ \text{1} \quad \text{---} \quad \text{---} \quad \text{2} \end{array}$$

while

$$\rho_\alpha \rho_\beta D_{\alpha\beta}^{(2)}(r) = \begin{array}{c} \text{---} \text{---} \text{---} \\ \text{1} \quad \text{---} \quad \text{2} \end{array} + \begin{array}{c} \text{---} \text{---} \text{---} \text{---} \\ \text{1} \quad \text{---} \quad \text{---} \quad \text{2} \end{array} + \begin{array}{c} \text{---} \text{---} \text{---} \text{---} \\ \text{1} \quad \text{---} \quad \text{---} \quad \text{2} \end{array} + \begin{array}{c} \text{---} \text{---} \text{---} \text{---} \\ \text{1} \quad \text{---} \quad \text{---} \quad \text{2} \end{array} + \begin{array}{c} \text{---} \text{---} \text{---} \text{---} \\ \text{1} \quad \text{---} \quad \text{---} \quad \text{2} \end{array} + \begin{array}{c} \text{---} \text{---} \text{---} \text{---} \\ \text{1} \quad \text{---} \quad \text{---} \quad \text{2} \end{array} + \begin{array}{c} \text{---} \text{---} \text{---} \text{---} \\ \text{1} \quad \text{---} \quad \text{---} \quad \text{2} \end{array} + \begin{array}{c} \text{---} \text{---} \text{---} \text{---} \\ \text{1} \quad \text{---} \quad \text{---} \quad \text{2} \end{array}$$

These chains are to be added by the use of the hypercircle

$$\begin{aligned} F_{D\alpha\beta}(1,2) &= \rho_\alpha \delta_{\alpha\beta} \delta(1,2) + \rho_\alpha \rho_\beta h_{D\alpha\beta}(1,2) \\ &= \bullet + \text{---} \bullet = \text{---} \bullet \end{aligned} \quad (12.17)$$

$F_D$  depends only on the difference between its two arguments for the potentials we are considering. We now have

$$\begin{aligned} \rho_\alpha \rho_\beta D_{\alpha\beta}^{(1)}(r) &= \begin{array}{c} \text{---} \text{---} \\ \text{1} \quad \text{---} \quad \text{2} \end{array} \\ \rho_\alpha \rho_\beta D_{\alpha\beta}^{(2)}(r) &= \begin{array}{c} \text{---} \text{---} \text{---} \text{---} \\ \text{1} \quad \text{---} \quad \text{---} \quad \text{2} \end{array} \end{aligned} \quad (12.18)$$

Note that the symmetry number of all the graphs in (12.15) are 1 and that for the purposes of calculating symmetry numbers, a hypercircle is to be treated as an ordinary circle. We can write  $\rho_\alpha \rho_\beta D_{\alpha\beta}^{(n)}(r)$  as a

chain of  $(n+1)$  hypercircles separated by  $n$   $\psi$ -bonds. We then define

$$\hat{\psi}_{\alpha\beta}(\underline{k}) = \int d\underline{r} \exp(-i\underline{k} \cdot \underline{r}) \psi_{\alpha\beta}(\underline{r}) ,$$

$$\hat{F}_{D\alpha\beta}(\underline{k}) = \int d\underline{r} \exp(-i\underline{k} \cdot \underline{r}) F_{D\alpha\beta}(\underline{r})$$

so that we have

$$\rho_{\alpha} \rho_{\beta} D_{\alpha\beta}^{(n)}(\underline{r}) = \frac{1}{(2\pi)^3} \int d\underline{k} e^{i\underline{k} \cdot \underline{r}} \left\{ [\hat{F}_D(\underline{k}) \psi(\underline{k})]^n \hat{F}_D(\underline{k}) \right\}_{\alpha\beta} . \quad (12.19)$$

To aid our summing the series (12.16) we define

$$P(\underline{k}) = \hat{F}_D(\underline{k}) \psi(\underline{k}) \quad (12.20)$$

(where  $\hat{F}_D$ ,  $\psi$  are square matrices of order the number of particle species in the system) so that we can sum (12.16) using (12.19) to obtain


$$\rho_{\alpha} \rho_{\beta} D_{\alpha\beta}(\underline{r}) = \frac{1}{(2\pi)^3} \int d\underline{k} e^{i\underline{k} \cdot \underline{r}} \left\{ P(\underline{k}) [1 - P(\underline{k})]^{-1} \hat{F}_D(\underline{k}) \right\}_{\alpha\beta}$$

Another useful quantity which is related to the renormalized potential is given by

$$\rho_{\alpha} \rho_{\beta} \Psi_{\alpha\beta}(1,2) = \left\{ \begin{array}{l} \text{THE SUM OF GRAPHS WITH TWO WHITE } \rho_1\text{-CIRCLES,} \\ \text{(ONE SPECIES } \alpha \text{ LABELLED 1, ONE SPECIES } \beta \\ \text{LABELLED 2) WHICH ARE CONNECTED BY TWO OR MORE} \\ \text{GENERALIZED CHAINS AND WHICH MAY OR MAY NOT} \\ \text{HAVE AN } h_D\text{-BOND BETWEEN THE WHITE CIRCLES.} \end{array} \right. \quad (12.22)$$

$$= [1 + h_{D\alpha\beta}(1,2)]$$

$$\times \left\{ \begin{array}{l} \text{THE SUM OF DIAGRAMS WITH TWO WHITE } \rho_1\text{-CIRCLES} \\ \text{(ONE SPECIES } \alpha \text{ LABELLED 1, ONE SPECIES } \beta \\ \text{LABELLED 2) WHICH ARE CONNECTED BY TWO OR MORE} \\ \text{GENERALIZED CHAINS.} \end{array} \right.$$

If we write a generalized chain as  and retain ----- for  $h_D$  then

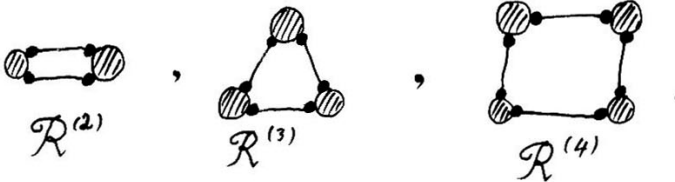
$$\begin{aligned} \psi_{\alpha\beta}(1,2) = & \text{[diagram 1]} + \text{[diagram 2]} + \text{[diagram 3]} + \dots \\ & + \text{[diagram 4]} + \text{[diagram 5]} + \text{[diagram 6]} + \dots \end{aligned}$$

The symmetry number for these graphs is (2.28)  $n!$  so that the series are just exponential series in  $D_{\alpha\beta}$  without the first two terms.

Thus

$$\psi_{\alpha\beta}(1,2) = [1+h_{D_{\alpha\beta}}(1,2)] \left\{ \exp[D_{\alpha\beta}(1,2)] - 1 - D_{\alpha\beta}(1,2) \right\} \quad (12.23)$$

We are now able to add up two more classes of perturbation diagrams: the RING diagrams, and the  $B_2$ -class. We consider the diagrams in the series for  $\mathcal{A}$  which are generalized rings of  $\psi$ -bonds connected by  $F_D$  hypercircles. The first few of these are



We define

$$|\Omega| \mathcal{A}_{\text{RING}} = \sum_{n=2}^{\infty} \mathcal{R}^{(n)} \quad (12.24)$$

Since the generalized rings are in fact polygons, their symmetry number is  $2n$  so that

$$\mathcal{R}^{(n)} = \frac{|\Omega|}{2n} \sum_{\alpha} \sum_{\beta} \rho_{\alpha} \rho_{\beta} \int d\mathbf{r} D_{\alpha\beta}^{(n-1)}(\mathbf{r}) \psi_{\beta\alpha}(\mathbf{r}) \quad (12.25)$$



since a generalized ring is a generalized chain whose ends have been joined by a  $\psi$ -bond. From (12.19) and (12.20) we then have, by viewing (12.25) as a Fourier transform at zero wave vector,

$$\mathcal{R}^{(n)} = \frac{1}{2n(2\pi)^3} |\Omega| \int d\mathbf{k} \text{Tr} [P(\mathbf{k})]^n \quad (12.26)$$





which on substitution into (12.24) gives

$$\mathcal{A}_{\text{RING}} = - \frac{1}{2(2\pi)^3} \int d\mathbf{k} \left\{ \text{Tr} P(\mathbf{k}) + \log \det[1-P(\mathbf{k})] \right\} \quad (12.27)$$

where we have used  $\log(1-x) = - \sum_{n=1}^{\infty} x^n/n$  to sum (12.24), and then

$\text{Tr} \log A = \log \det A$ , a matrix identity. The  $B_2$ -class of diagrams is

$$\begin{aligned} B_2 &= \text{---} \bullet \text{---} \bullet \text{---} + \text{---} \bullet \text{---} \bullet \text{---} + \text{---} \bullet \text{---} \bullet \text{---} + \text{---} \bullet \text{---} \bullet \text{---} + \text{---} \bullet \text{---} \bullet \text{---} + \dots \\ &= \frac{1}{2} \sum_{\alpha\beta} \rho_{\alpha} \rho_{\beta} \int d\mathbf{r} h_{D\alpha\beta}(r) \cdot \frac{1}{2} [D_{\alpha\beta}(r)]^2 \\ &\quad + \frac{1}{2} \sum_{\alpha\beta} \rho_{\alpha} \rho_{\beta} \int d\mathbf{r} g_{D\alpha\beta}(r) \sum_{n=3}^{\infty} \frac{1}{n!} [D_{\alpha\beta}(r)]^n \\ &= \frac{1}{2} \sum_{\alpha\beta} \rho_{\alpha} \rho_{\beta} \int d\mathbf{r} \psi_{\alpha\beta}(r) - \frac{1}{2} [D_{\alpha\beta}(r)]^2 \end{aligned} \quad (12.28)$$

We note that , a natural member of this class, has already been included as part of  in  $\mathcal{A}_{\text{RING}}$ . The remaining graphs in  $\mathcal{A}$  may have further replacements made in them, making use of the replacement theorem of section 8. In the resulting graphs we may have between each pair of circles an  $h_D$ -bond, a D-bond or a  $\psi$ -bond, and at most one of each type. Note that a  $\psi$ -bond may not occur with an  $h_D$  - or D-bond, that  and  are part of the D-bond sum and will

not occur and that there may be no reference articulation pairs of circles.

The result is

$$\mathcal{A} = \mathcal{A}_D + \mathcal{A}_{HTA} + \mathcal{A}_{RING} + B_2$$

$$+ \frac{1}{|\Omega|} \left\{ \begin{array}{l} \text{SUM OF ALL MORE THAN SINGLY CONNECTED GRAPHS WITH} \\ \text{NO WHITE CIRCLES, THREE OR MORE BLACK } \rho_1\text{-CIRCLES} \\ h_D\text{-, D- AND } \psi\text{-BONDS, NO MORE THAN ONE BOND OF ANY} \\ \text{TYPE BETWEEN TWO CIRCLES, NO } \psi\text{-BOND BETWEEN ANY TWO} \\ \text{CIRCLES CONNECTED BY ANOTHER BOND, NO BLACK CIRCLES} \\ \text{WITH ONLY A D-BOND AND AN } h_D\text{-BOND ATTACHED TO IT,} \\ \text{NO REFERENCE ARTICULATION PAIRS OF CIRCLES AND AT} \\ \text{LEAST TWO } \psi\text{-BONDS OR TWO D-BONDS OR ONE } \psi\text{- AND ONE} \\ \text{D-BOND.} \end{array} \right. \quad (12.29)$$

A similar reduction and partial summation of the graphical expansion of  $h_{2\alpha\beta}(1,2)$  is possible, using the same bonds. The reduction works in the same way and so will not be given here. The result is

$$\rho_\alpha \rho_\beta h_{2\alpha\beta}(1,2) = \rho_\alpha \rho_\beta \left\{ h_{D\alpha\beta}(1,2) + D_{\alpha\beta}(1,2) + h_{D\alpha\beta}(1,2) D_{\alpha\beta}(1,2) + \psi_{\alpha\beta}(1,2) \right\}$$

$$+ \left\{ \begin{array}{l} \text{THE SUM OF ALL CONNECTED GRAPHS WITH TWO WHITE } \rho_1\text{-CIRCLES} \\ \text{(ONE SPECIES } \alpha \text{ LABELLED 1, ONE SPECIES } \beta \text{ LABELLED 2)} \\ \text{AT LEAST ONE BLACK } \rho_1\text{-CIRCLE, } h_D\text{-, D- AND } \psi\text{-BONDS, NO} \\ \text{ARTICULATION CIRCLES AND NO } \text{REF+REDUC} \text{ ARTICULATION PAIRS OF CIRCLES} \\ \text{THE SAME RESTRICTIONS ON THE NUMBERS OF BONDS CONNECTING} \\ \text{ANY PAIR OF CIRCLES OR ATTACHED TO ANY ONE BLACK CIRCLE} \\ \text{AS IN (12.28) AND AT LEAST ONE D- OR } \psi\text{-BOND.} \end{array} \right. \quad (12.30)$$

The power of the replacement theorems is seen in these last two results, where the number of graphs has been greatly reduced.

The great virtue of the Andersen and Chandler theory is that (as one can see from (12.14) and (12.27)) the quantity

$$\mathcal{A}_D + \mathcal{A}_{HTA} + \mathcal{A}_{RING} + B_2 \quad (12.31)$$

depends on the value of the perturbation potential  $v_{\alpha\beta}(r)$  inside the hard sphere. Since this function is arbitrary, we can minimize

$$\mathcal{A} - (\mathcal{A}_D + \mathcal{A}_{HTA} + \mathcal{A}_{RING} + B_2)$$

or

$$\mathcal{A} - (\mathcal{A}_D + \mathcal{A}_{HTA} + \mathcal{A}_{RING})$$

with respect to  $v_{\alpha\beta}(r)$  inside the hard core. Thus we may optimize the accuracy of the approximation (12.31) to  $\mathcal{A}$ . The expansion (12.29) is closely related to that of Stell and Lebowitz<sup>[48]</sup> for coulombic fluids and are generalizations of the cluster expansions of Friedman<sup>[49]</sup> where the perturbation is coulombic for all  $r$ . However, the present expansion is superior to these approaches because of the optimization of accuracy possible.

From the functional differentiation result (3.6) and the definitions of  $\mathcal{A}_{RING}$  and  $D_{\alpha\beta}(r)$ , we have

$$\delta|\Omega| \mathcal{A}_{RING} / \delta(-v_{\alpha\beta}(r)/kT) = \frac{1}{2} \rho_\alpha \rho_\beta D_{\alpha\beta}(r) \quad (12.32)$$

Andersen and Chandler propose choosing  $v_{\alpha\beta}(r)$  for  $r < R_{\alpha\beta}$  so that

$$D_{\alpha\beta}(r) = 0 \quad r < R_{\alpha\beta} \quad (12.33)$$

It is fairly easy to show from (12.27) that  $\check{V}_{\alpha\beta}^{\text{RING}}$  is a positive definite functional of  $v_{\alpha\beta}(r)$  for  $0 < r < R_{\alpha\beta}$ . Thus it is possible to find a value of  $v_{\alpha\beta}(r)$  on  $0 < r < R_{\alpha\beta}$  for which (12.33) is satisfied. They also give arguments to show that (12.33) does indeed enhance the accuracy of the approximation (12.31) considerably. They show the connection between this theory and the mean spherical model is given by

$$g_{2\alpha\beta}^{(\text{MSM})}(r) = g_{D\alpha\beta}^{(\text{PY})}(r) + D_{\alpha\beta}^{(\text{PY})}(r) \quad (12.34)$$

where  $g_{D\alpha\beta}^{(\text{PY})}$  is the two particle correlation function for hard spheres in the Percus-Yevick approximation and  $D_{\alpha\beta}^{(\text{PY})}$  is  $D_{\alpha\beta}$  calculated using  $g_{D\alpha\beta}^{(\text{PY})}$  instead of  $g_{D\alpha\beta}$ , and using the perturbation that makes

$$D_{\alpha\beta}^{(\text{PY})}(r) = 0 \quad r < R_{\alpha\beta} \quad (12.35)$$

In a later paper<sup>[50]</sup> Andersen, Chandler and Weeks show that their optimization procedure gives good agreement for ionic systems with computer approximations.

In this section we have shown how the perturbation ideas introduced in the last section and the graph theory developed earlier is used to develop a perturbation theory. We hope the exercise will be instructive to some of our readers.

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