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On Mayer's Theory of Cluster Expansions*

EDWIN E. SALPETER

Newman Laboratory of Nuclear Studies, Cornell University, Ithaca, New York

New derivations are presented for Mayer's well-known irreducible cluster expansions (in powers of the density) for the fugacity, for the two-body correlation function and for the n-body correlation function. These derivations are based on the assumption that all the cluster expansions converge (and are thus not suitable for investigating condensation phenomena) but shortcircuit much of the combinatorial algebra encountered in previous derivations, by means of relatively simple topological arguments.

An expansion is derived for the two-body correlation function for a system involving long-range but weak two-body forces. The first term of this expansion reduces to the Debye-Hückel theory for the special case of Coulomb forces. This expansion differs slightly from one derived previously by Mayer and the problem of analytic continuation, encountered when proceeding to the Coulomb force, is treated differently. Topological methods are outlined for rederiving some integral equations of Kirkwood and Salsburg and of Mayer and Sarolea.

1. INTRODUCTION

A large class of problems in classical statistical mechanics deals with the equation of state and with the two-body (or n-body) correlation function for a system containing a very large number of atoms, molecules or ions. For a gas consisting of neutral molecules, Mayer's method of cluster expansions (*1–3*) is eminently successful. In this method one first derives infinite (reducible-cluster) expansions involving powers of the fugacity Z. Finally one derives infinite (irreducible-cluster) expansions in powers of the density ρ (not involving powers of Z) both for the fugacity (*1*) and for the n-body correlation function (*2*). For low enough densities these expansions converge rapidly, even if the repulsive potential between two molecules at short distances is very strong, as long as the interaction potential falls off rapidly enough at large distances, which is the case for neutral molecules.

However, if the long-range Coulomb potential is acting between the constituent ions and electrons in a solution of electrolytes or in a plasma, this cluster expansion breaks down however low the density is. An approximate method for

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treating systems involving Coulomb interactions, valid only in the limit of low density, was proposed a long time ago in the classic paper by Debye and Hückel (*4*). More recently a number of authors (*5–9*) have developed methods which contain the Debye-Hückel results as a first approximation but are capable (at least in principle) of yielding corrections for the density being finite. These various methods have some features in common; in particular, integral equations involving the two-body correlation function and more complicated functions than simple powers of the density occur.

In a system containing neutral molecules without long-range forces, condensation phenomena take place if the density is high enough. For such densities the cluster expansions, at least in their simplest form, again break down. Although no entirely satisfactory statistical mechanical treatment of liquids or of condensation phenomena exists at the moment, a large number of attempts have been made. Of these diverse methods, many make use of various integral equations involving again the two-body (and n-body) correlation function. References to the voluminous literature will be found in the reviews by De Boer (*10*), Green (*11*), and Hill (*12*).

The purpose of the present paper is largely methodological: First of all we shall rederive Mayer's well-known expansion in terms of irreducible clusters, both for the fugacity and for the n-body correlation function, by means of a new method (Sections 2, 3, and 4). In this method much of the combinatorial algebra involved in the more standard derivations is replaced by simple topological considerations relating to Mayer's cluster diagrams. After that we shall derive various other expressions which involve integral equations as well as expansions (Sections 5, 6, and 7). Most of these expressions are not new, but are derived by a method which again circumvents much of the combinatorial work. This is achieved by topological considerations on possible regroupings of the various cluster diagrams.

The author should perhaps apologize in advance for writing a paper which, in some ways, represents several steps backwards: Many of the results are not new, some more powerful techniques and more general results have been developed previously and some of the methods of derivation used in the present paper are less rigorous than previous derivations. Nevertheless it is hoped that, in a subject beset by complicated notation and difficult mathematical proofs, the simple-minded and unrigorous derivations of previously known expressions might be of some help in the future search for new expressions and relations.

In the remainder of this section we explain the notation and the restrictions used. We consider a system of volume V and temperature T consisting of N particles, all of the same mass m and similar properties and with a central interaction potential $U(r_{ij})$ acting between any pair i,j of the particles. We assume classical mechanics holds and that no many-body forces act. We make no restrictions against two-body potentials $U(r)$ which become positively (repulsive) infinite at small distances r, but assume $U(r)$ does not equal minus infinity anywhere. We assume at the moment that $U(r)$ falls off more rapidly than r^{-3} at large distances. We shall consider the special case of the long-range Coulomb potential only in Section 5.

Since we are dealing with classical mechanics the momentum space integrals in the macrocanonical partition function for the N particles can be integrated immediately and the Helmholtz free energy, A, can be written (*1, 12*) in the form

$$A(N,V,T) = -kT \ln [(2\pi mkT/h^2)^{3N/2} (V^N/N!)Q(N,V,T)]. \tag{1.1}$$

The symbol $Q(N,V,T)$, which we shall often abbreviate to Q_N, stands for the configuration integral

$$Q(N,V,T) = V^{-N} \int \cdots \int d1\, d2 \cdots dN \exp\cdot[- \sum_{1 \leqq i < j \leqq N} u_{ij}]. \tag{1.2}$$

We have used the abbreviation

$$u_{ij} \equiv U(r_{ij})/kT$$

and $\int dj$ denotes integration of the position coordinate of particle j over the volume V. The only term to be evaluated in expression (1.1) for the free energy A is the function $Q(N,V,T)$. This function Q is normalized so that it equals unity if u_{ij} is zero, i.e., for the trivial case of no interaction. We are considering potentials $U(r)$ of finite range and will be interested in the variation of the function Q with particle density $\rho \equiv N/V$ for extremely large values of the volume V. For such finite range potentials the integral $Q(N,V,T)$ approaches unity as ρ approaches zero for any finite and fixed value of N (V approaching infinity).

Instead of evaluating $Q(N,V,T)$, and hence the free energy A, directly we shall only consider the variation of Q_N with the particle number N, keeping V and T fixed. This variation can be expressed in terms of the chemical potential μ or the fugacity Z or the concentration activity coefficient γ. These quantities are related to each other in a simple manner and are defined by

$$\begin{gathered} \mu \equiv \left(\frac{\partial A}{\partial N}\right)_{V,T} = kT[\ln Z_N - \ln (2\pi mkT/h^2)^{3/2}]; \\ Z_N \equiv \rho\gamma_N ; \qquad \ln \gamma_N = -\frac{d \ln Q_N}{dN}, \qquad \gamma_N = \frac{Q_{N-1}}{Q_N} \end{gathered} \tag{1.3}$$

where $\rho = N/V$ is again the particle density. We are only considering systems with no long-range order in the limit of N and V very large, but with the density $\rho = N/V$ finite. In such cases γ (or Z or μ) as a function of N,V,T depends only on the two variables ρ and T. Even though we do not yet have explicit expressions involving the pressure, a knowledge of γ (or Z or μ) as a function of ρ and T is sufficient for determining all other thermodynamic functions: Using the fact that Q_N (and also γ) approaches unity as the density ρ approaches zero, we have for any finite ρ

$$\ln Q(N,V,T) = -\int_0^N \ln \gamma(N',V,T)\, dN' = -V \int_0^\rho \ln \gamma(\rho',T)\, d\rho'. \qquad (1.4)$$

The integral (1.4) thus determines the Helmholtz free energy A as a function of N, T and of V (or ρ). From this free energy function A all other thermodynamic functions can be calculated, such as energy, entropy and the pressure P as a function of ρ and T (equation of state). We give just a few examples of explicit expressions for thermodynamic functions in terms of the concentration activity coefficient γ: From the general relation

$$\frac{\partial P(\rho,T)}{\partial \rho} = \rho \frac{\partial \mu(\rho,T)}{\partial \rho}$$

and the fact that the pressure approaches zero when the density does, we find for the equation of state

$$P(\rho,T) = kT\left[\rho + \int_0^\rho d\rho' \rho' \frac{\partial \ln \gamma(\rho',T)}{\partial \rho'}\right] \qquad (1.5)$$

We also know that the Gibbs free energy function $F(N,T,P)$ is simply equal to $N\mu$, where μ is given in (1.3). In this expression for F the density ρ can be eliminated in favor of the pressure P by means of the equation of state (1.5). For those special cases for which the Taylor expansion in powers of ρ for the logarithm of the function $\gamma(\rho,T)$ converges, i.e.,

$$\ln \gamma(\rho,T) = -\sum_{k=1}^{\infty} \beta_k(T)\rho^k,$$

the equation of state (1.5) reduces to

$$P(\rho,T) = kT\rho\left[1 - \sum_{k=1}^{\infty} \frac{k}{k+1} \beta_k(T)\rho^k\right], \qquad (1.5a)$$

the well-known virial expansion.

We define next the n-body correlation function F_n and the potential of mean force w_n by

$$\begin{aligned} F_n(1, 2, \cdots n) &\equiv \exp[-w_n(1, 2, \cdots n)] \\ &= Q_N^{-1} V^{n-N} \int \cdots \int d(n+1) \cdots dN \exp[-\sum_{1 \leqq i < j \leqq N} u_{ij}]. \end{aligned} \qquad (1.6)$$

In this expression $\sum u_{ij}$ includes the particles 1 to n but their positions are to be considered fixed at r_1, r_2, $\cdots$ r_n. We are considering only a system without long-range order of volume infinitely large compared with the potential range. The function F_n is thus invariant to a displacement of the group of n particles as a whole and depends only on the $n - 1$ vector distances r_{12}, r_{23}, $\cdots$ $r_{n-1,n}$ between the particles. For a single particle, in particular, we have $F_1(1) = 1$, $w_1(1) = 0$. If the interaction potential $U(r)$ is spherically symmetrical the two-body correlation function $F_2(1,2) = F_2(r_{12})$ depends only on the radial separation r_{12} between the two particles. A number of alternative definitions of a n-body correlation function will be found in the literature, which differ from each other by terms of relative order n/N. With the definition (1.5) we adopt here we have exactly

$$F_{n-1}(1,2, \cdots n - 1) = V^{-1} \int dn\, F_n(1,2, \cdots n - 1, n). \tag{1.7}$$

We shall see that F_n approaches a constant value if particles 1 to $n - 1$ are fixed and the particle n moves far away from the other $n - 1$ particles. This limit which F_n approaches differs from F_{n-1} only by terms of order n/N. In particular, if all the n particles are very far from each other, F_n differs from unity only by terms of order n^2/N. For most purposes of this paper we shall be interested in moderate values of n and shall be able to neglect these small differences.

The two-body correlation function $F_2(1,2) = F_2(r_{12})$ is of course of interest in its own right. In addition a knowledge of it, or rather a slight generalization of it, is also sufficient for determining the concentration activity coefficient γ and hence the fugacity (see Ref. *12*, p. 193): We define a generalization of the configuration integral Q_N, the coefficient γ and the correlation function $F_2(1,j)$ as follows. We consider particle 1 endowed with a "charging parameter" ξ_1 but leave the other $N - 1$ particles unaltered. More specifically, we define $Q_N(\xi_1)$ by the expression (1.2) but with u_{ij} replaced by $\xi_1 u_{ij}$ and all the other u_{ij} unaltered. We shall denote $Q_{N-1}/Q_N(\xi_1)$ by $\gamma(\xi_1)$. We define a function $F_2(1,j;\, \xi_1) = F_2(r_{1j}\,;\, \xi_1)$ in an analogous manner, namely

$$F_2(1,2;\, \xi_1) = Q_N^{-1}(\xi_1) V^{2-N} \int \cdots \int d3 \cdots dN \exp\,[-\textstyle\sum \xi_i \xi_j\, u_{ij}] \tag{1.8}$$

with $\xi_i = 1$ for $i \neq 1$. For the special case $\xi_1 = 1$ we have of course $Q_N(\xi_1) = Q_N$, $\gamma(\xi_1) = \gamma$ and $F_2(1,2;\, \xi_1) = F_2(1,2)$. For the special case $\xi_1 = 0$ the particle 1 does not interact with any other particle and we have $Q_N(\xi_1) = Q_{N-1}$, $\gamma(\xi_1) = 1$ and $F_2(1,2;\, \xi_1) = F_1(2) = 1$. From these definitions one easily obtains

$$\frac{d \ln \gamma(\xi_1)}{d\, \xi_1} = V^{-1} \sum_{j=2}^{N} \int dj u_{1j} F_2(1,j;\, \xi_1)$$

and, approximating $N - 1$ by N,

$$\ln \gamma = \rho \int_0^1 d\xi \int d^3 r u(r) F_2(r; \xi), \tag{1.9}$$

where $u(r) = U(r)/kT$ as before.

2. MAYER'S CLUSTER EXPANSION FOR THE FUGACITY

The main aim of this section is to derive the well-known virial expansion for the fugacity Z (or, rather, for its logarithm) by a somewhat unorthodox method. This expression for $\ln Z$ is an expansion in powers of the density ρ with Mayer's irreducible cluster integrals $\beta_k(T)$ as coefficients. Before deriving this expression, we first rederive another well-known expression, the expansion for the density in powers of the fugacity with reducible cluster integrals as coefficients. We shall make formal use of this expression in our derivations of subsequent expressions.

We consider the volume V and the temperature as fixed and shall investigate expressions for γ_N^{-1}, the inverse of the activity concentration coefficient, defined by Q_N/Q_{N-1} where Q_N is given by the integral in (1.2). Let us label the extra particle occurring in Q_N as particle 1, those present both in Q_N and Q_{N-1} as 2 to N. Following Mayer we split the integrand in the integral occurring in (1.2) into the following sum

$$\exp\left[-\sum_{1 \leqq i < j \leqq N} u_{ij}\right] = 1 + \sum_{\alpha} f_\alpha + \frac{1}{2} \sum_{\alpha \neq \beta} f_\alpha f_\beta + \cdots ; \qquad f_\alpha \equiv f_{ij} = e^{-u_{ij}} - 1 \tag{2.1}$$

In (2.1) the symbol α (or β) stands for any one of the $N(N - 1)/2$ pairs of particles (ij) and the sum consists of $2^{N(N-1)/2}$ terms corresponding to the possible presence or absence of any of these pairs. Each of these terms can be represented graphically by a diagram which contains one line connecting a pair of points labelled i and j for each factor f_{ij} present in this particular term in the sum (2.1). For a potential of finite range the factor f_{ij} approaches zero rapidly as the separation r_{ij} becomes very large compared with the range.

The various diagrams and the corresponding terms in (2.1) can be classified and simplified as follows. For any diagram there is a unique number, say l, of points which are at least singly connected to point 1 (i.e., connected either directly by a line representing a factor in (2.1) or indirectly by an unbroken succession of lines passing through some of the other $l - 1$ points). The part of this diagram which involves the $l + 1$ singly connected points (including the point 1) is called a single "cluster". The remaining $N - l - 1$ points in our complete diagram may be connected to each other in any manner (or not at all), but none of these $N - l - 1$ points can be connected (directly or indirectly) to any of the $l + 1$ points of the cluster which contains point 1 (if any did, they would be at

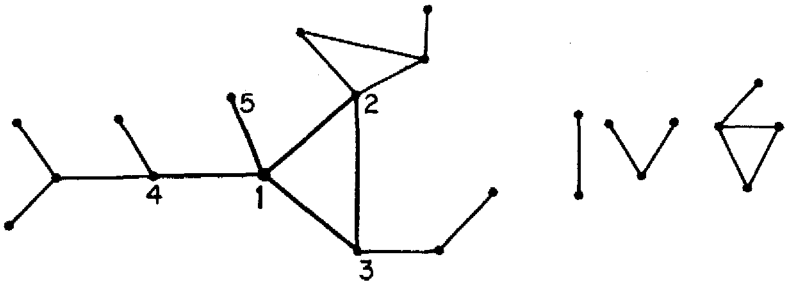

FIG. 1. An example of a general diagram—reducible cluster plus disconnected parts.

least singly connected to point 1 and would thus be part of the cluster). Figure 1 is an example of a diagram with 23 points which includes a cluster with $l = 14$. We consider now the contribution to the integral for Q_N in (1.2) of the term which corresponds to a particular diagram consisting of a given cluster (connecting particle 1 with l given particles 2 to $l + 1$) plus some configuration of the remaining $N - l - 1$ particles which are disconnected from the cluster. This integral reduces to the product of two simpler integrals: One is the integral

$$I_{l+1} = V^{-(l+1)} \int d1 \cdots d(l+1) \prod f_{ij}$$

with those f_{ij} included which correspond to lines in the cluster diagram; the other is an integral over the remaining $N - l - 1$ particles. We can now consider together all the diagrams in which the first integral I_{l+1} (with given particles 1, 2, $\cdots l + 1$) is exactly the same, but with all possible configurations for the $(N - l - 1)$-dimensional integral which multiplies I_{l+1}. From the identity (2.1) it follows that the sum of all the possible $(N - l - 1)$-dimensional integrals is simply

$$V^{-N+l+1} \int d(l+2) \cdots dN \exp\left[-\sum_{l+2 \leqq i < j \leqq N} u_{ij}\right] = Q_{N-l-1},$$

a configuration integral of form (1.2) with the same values of V and T but $N - l - 1$ particles instead of N.

These diagrams together then contribute an amount of $I_{l+1}Q_{N-l-1}$ to the expression for Q_N. Next we multiply I_{l+1} by the factor $(N - 1)!/!(N - l - 1)!$ to take care of the fact that any l particles of the $N - 1$ particles (besides the singled out particles 1) can be the companions of particle 1 in the cluster. We define the Mayer cluster integral b_l by

$$b_{l+1} = \frac{1}{(l+1)!V} \sum^{(l+1)} \int d1 \cdots d(l+1) \prod f_{ij} = \frac{V^l}{(l+1)!} \sum^{(l+1)} I_{l+1}, \tag{2.2}$$

where the symbol $\sum^{(l+1)}$ denotes summation over all the possible single cluster diagrams which can be formed from $l + 1$ given particles. Then

$$[V^{-l}(N-1)!/(N-l-1)!](l+1)b_{l+1}\,Q_{N-l-1}$$

is the total contribution to Q_N from all diagrams in which the particle 1 occurs in a cluster involving l other particles. In order to include all the $2^{n(n-1)/2}$ diagrams we now merely have to sum this expression over all values of l from zero to $N - 1$. Noting that

$$\frac{N-\nu}{V}\cdot\frac{Q_{N-\nu-1}}{Q_{N-\nu}} = Z_{N-\nu},$$

the fugacity for density $[(N - \nu)/N]\rho$, we finally obtain

$$\frac{1}{\gamma_N} \equiv \frac{N}{VZ_N} \equiv \frac{Q_N}{Q_{N-1}} = \sum_{l=0}^{N-1}(l+1)b_{l+1}\prod_{\nu=1}^{l} Z_{N-\nu}. \tag{2.3}$$

The expression (2.3) is exact and holds for all values of N. The right-hand side of (2.3) for Z_N depends only on the fugacity Z for particle numbers $(N - \nu)$ smaller than N (besides depending on the cluster integrals b_l). By the repeated use of this recursion relation (2.3) for $Z_{N-\nu}$, etc., one could derive an explicit expression for Z_N in the form of a multiple sum involving only the b_l and known functions of N and V. This expression would be exact and applicable whether we are dealing with condensed systems or not and might therefore be useful for investigating condensation phenomena. This expression, however, is probably too complicated for practical applications. If we restrict ourselves to low enough densities where no condensation is possible, i.e., we assume that the sum in (2.3) converges rapidly, this expression simplifies considerably. For such systems we let N and V tend to infinity, keeping the density $\rho = N/V$ finite, and assume that even in this limit only terms with finite values of l are of any importance in the sum (2.3). Since $Z_{N-\nu}$ is a smoothly varying function of $(N - \nu)/V$, we can in this limit replace $Z_{N-\nu}$, Z_{N-l}, etc., by Z_N. Dropping the subscript N, we then have

$$\begin{aligned}\rho &= \sum_{l=1}^{\infty} l b_l Z^l,\\ \gamma^{-1} &= \sum_{l=0}^{\infty}(l+1)b_{l+1}\rho^l\gamma^l.\end{aligned} \tag{2.4}$$

In the limit of $V, N \to \infty$ but with finite l, the cluster integrals b_l depend only on temperature but not on V or density ρ and (2.4) can be thought of as an expansion for ρ in powers of Z.

We come now to the expansion for $1/Z$ (or its logarithm) in powers of the density with Mayer's irreducible cluster-integrals β_k as coefficients. In the orthodox derivation of this expression, the b_l are first expressed in terms of the β_k and the expansion in (2.4) is then inverted. Instead we shall derive an expression for $1/\gamma$ by a method somewhat similar to that which leads to (2.3), but with terms regrouped in a somewhat different manner. This method will give the desired result without much labor, but we shall have to restrict ourselves at the start to cases where the cluster-expansion converges rapidly; our derivation will thus be unsuitable for considering condensation phenomena.

We have already seen that many of the terms in the expansion (2.1) when substituted into the integral (1.2) can be written as the product of several independent integrals, each one corresponding to one cluster integral. Many of these cluster integrals further reduce to the product of even simpler independent integrals. Consider a cluster diagram with $l + 1$ points which can be split into two or more disconnected diagrams by "snipping" the diagram at a single point. In the corresponding integral in (1.2) carry out the integration over the position $\mathbf{r}_s$ of the "snipped" particle last and in the other l integrations use the coordinates of the other points relative to this one, $(\mathbf{r}_i - \mathbf{r}_s)$, as the variables of integration. With $\mathbf{r}_s$ fixed, the $3l$-dimensional integral for such a "reducible cluster" is then the product of two or more independent integrals. In principle, these independent integrals depend on the position $\mathbf{r}_s$ relative to the boundaries of the volume V. However, if we restrict ourselves to finite values of the number l of particles, to potentials of finite range and proceed to the limit $V \to \infty$, then this dependence on $\mathbf{r}_s$ is eliminated, the last integration over $\mathbf{r}_s$ simply gives a multiplicative factor of V and the $3(l + 1)$-dimensional integral in (1.2) is strictly the product of two or more independent integrals.

We call a cluster diagram containing k points besides our singled out point 1, which cannot be reduced further by "snipping" at any single one of the $(k + 1)$ points, a "simple irreducible cluster". Mayer's "irreducible cluster integrals" β_k are defined by

$$\beta_k = (1/k!) \int \cdots \int d2 \cdots d(k+1) \ \sum\nolimits^{(k)} \prod f_{ij} , \tag{2.5}$$

where the symbol $\sum^{(k)}$ denotes summation over all possible irreducible cluster diagrams which can be formed with $k + 1$ given particles. For $k = 0$, the particle 1 is not connected to any other point and $\beta_0 \equiv 1$. For $k = 1, 2, 3$ the corresponding diagrams are given in Fig. 2 (to the left of the first dotted line) and we have

$$\begin{aligned}\beta_1 &= \int d2 f_{12} ,\\ \beta_2 &= \frac{1}{2} \iint d2\, d3 f_{12} f_{23} f_{31} , \\ \beta_3 &= \frac{1}{6} \iiint d2\, d3\, d4 f_{12} f_{23} f_{34} f_{41} (3 + 6 f_{\underset{13}{\cancel{12}}} + f_{13} f_{24}).\end{aligned} \tag{2.6}$$

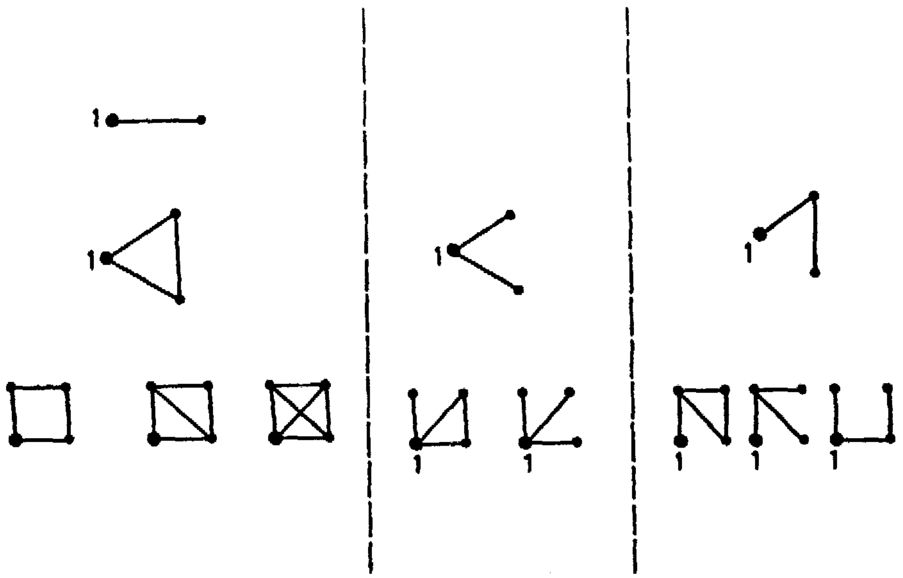

FIG. 2. From left to right: Simple 1-irreducible clusters; general 1-irreducible clusters 1-reducible clusters. The diagrams with $k = 1, 2, 3$ are shown.

The factors 3 and 6 which occur in β_3, for instance, are the number of possible permutations of the four numbered points which lead to distinguishable diagrams but of the same kind of integral (for more detail, see Ref. *1*, p. 286). Since we are restricting ourselves to finite values of k with $V \rightarrow \infty$ for potentials of finite range, each cluster integral $\beta_k(T)$ is independent of volume V (or density ρ). We shall also find it useful to define a class of diagrams intermediate in complexity between the "simple irreducible" and reducible clusters: We shall call a cluster diagram with k points plus the singled out point 1 a "general 1-irreducible cluster" if it cannot be reduced to two or more separate clusters by "snipping" at any of the k points (other than point 1), whether it can be reduced by snipping at point 1 or not. These diagrams thus include all the "simple irreducible" ones plus some additional ones. In Fig. 2 all the diagrams to the left of the second dotted line belong to the class of "general 1-irreducible clusters". We define "general 1-irreducible cluster integrals" β_k' in complete analogy with (2.5). For $k = 1, 2, 3$ we have

$$\begin{aligned}\beta_1' &= \beta_1,\\ \beta_2' &= \beta_2 + \frac{1}{2!}\beta_1^2,\\ \beta_3' &= \beta_3 + \frac{3}{3!}\beta_2\beta_1 + \frac{1}{3!}\beta_1^3.\end{aligned} \tag{2.7}$$

The definitions of the various types of clusters can also be phrased in more topological language: A general (reducible) cluster is a diagram in which all pairs of points are at least singly connected. A "general 1-irreducible cluster", with k points (which we shall call field-points) besides point 1, is defined by the condition that each of the k field-points is either "multiply connected" to point 1 or else it is directly connected only to point 1 and to no other point. By a "multiple connection" between two points we mean that there are at least two different continuous paths between them with *no* intermediate points common to the two paths. Finally, a "simple 1-irreducible cluster" with $k \geqq 2$ can be defined by the two conditions that (i) each field-point is multiply connected to point 1, and (ii) for each pair of field-points there is at least one path not passing through point 1 which connects them. One can show[1] that conditions (i) plus (ii) are equivalent to the single condition (iii): Each of the $k + 1$ points is multiply connected to every other point. The term β_1 for $k = 1$ is, however, also included among the irreducible clusters (being a one-dimensional integral, it cannot be reduced further), even though there is only a single line in this "cluster".

An example of the various stages of reduction possible for a complex diagram is given in Fig. 1. This diagram with 23 points can first be reduced to a reducible cluster diagram with 14 points (including the point 1). This cluster can further be reduced to a "general 1-irreducible cluster" containing the points 1 to 5, by simply "snipping" at points 2, 3, and 4. Finally this five-point cluster can be reduced to three separate "simple irreducible clusters" (1,2,3), (1,4) and (1,5) by snipping at the singled-out point 1. The total number of simple irreducible clusters with a given number $k + 1$ of points is much smaller than the number of general (reducible) clusters with the same number of points, $l = k + 1$, for large k. Nevertheless even the number of simple irreducible clusters increases very rapidly with k for large k. We shall not discuss in this paper the question of convergence of the sequence of numbers β_k or their explicit evaluation.

Having defined the cluster integrals β_k and β_k' we can now start on the derivation of the expansion for $1/\gamma$ in powers of the density. We again write $1/\gamma_N = Q_N/Q_{N-1}$ and expand the expression (1.2) for Q_N by means of the identity (2.1) and single out particle 1 as the extra particle present in Q_N but not in Q_{N-1}. We reclassify the totality of general (reducible) cluster diagrams which contain the point 1 in the following manner: For each such diagram there is a unique "general 1-irreducible cluster" with k points, say, in addition to point 1, to which this diagram could be reduced (we shall call these k additional points "field-points". We consider now all the diagrams which contain a particular

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[1] To outline the derivation: It follows from (i) that there are at least two paths, a and b, connecting a pair of field-points ij with at most point 1 common to the two paths. If both paths a and b pass through point 1, then (ii) ensures that some point (possibly i) on "one side" of point 1 is connected to some point (possibly j) on "the other side" by some link not passing through any of the points of paths a and b. From this it follows that i and j are multiply connected, i.e., that (iii) holds. The inverse, i.e., that (i) and (ii) follow from (iii), is obvious.

"general 1-irreducible cluster" with point 1 plus the given field-points 2, 3, $\cdots$, k. A typical term in this collection of diagrams can be built up as follows: We add to the fixed "1-irreducible cluster" any kind of cluster diagram (reducible or not but at least singly connected) *containing* l_2 points besides the point 2, attached at the point 2 only. We next attach at the single point 3 any kind of cluster diagram with l_3 points (plus the point 3); and so on for all field-points 2 to $k + 1$. Note that we do *not* need to attach any diagram at point 1, since all possible junctions at point 1 will be accounted for by considering "general 1-irreducible clusters" rather than "simple irreducible" ones. The reducible cluster diagram in Fig. 1, for instance, has $k = 4$ with $l_2 = 3$, $l_3 = 2$, $l_4 = 4$ and $l_5 = 0$ (i.e., no diagram attached at point 5 at all). In evaluating the contribution to Q_N from one of these typical cluster diagrams with

$$\left[\sum_{\nu=2}^{k+1} (l_\nu + 1) + 1\right]$$

points we assume immediately that $\sum (l_\nu + 1) \ll N$ and consequently replace terms like $(N - 1)!/L!(N - L - 1)!$ by $N^L/L!$, γ_{N-L} by γ_N (which we simply call γ) and Z_{N-L} by Z_N (which we call Z), where L is any number of the order of $\sum^{k+1} (l_\nu + 1)$ or less. Repeating the arguments which lead to (2.2), (2.3), and (2.4) and, remembering the fact that reducible cluster integrals can be written as the product of irreducible ones, we get for the contribution to Q_N from our typical cluster diagram[2] (after permutation over the possible numberings of all particles other than particle 1)

$$N^L V^{-L} \beta_k' \prod_{\nu=2}^{k+1} b_{l_\nu+1}(l_\nu + 1); \qquad L \equiv \sum_{\nu=2}^{k+1} (l_\nu + 1).$$

This contribution has to be multiplied by Q_{N-L-1}, to take account of all the disconnected graphs that can be formed from the remaining $N - L - 1$ points, and to be divided by Q_{N-1} to represent the contribution to $1/\gamma$ (rather than to Q_N). Since we replace Q_{N-L}/Q_N by γ^L in our approximation, our typical term in the expansion for $1/\gamma$ is then

$$\rho^k \beta_k' \gamma^k \prod_{\nu=2}^{k+1} (l_\nu + 1) b_{l_\nu+1} \rho^{l_\nu} \gamma^{l_\nu}, \tag{2.8}$$

where $\rho = N/V$ and $\beta_0' = b_1 = 1$. It will be noted *that each of the factors in* the product over ν in (2.8) equals the contribution which the diagram attached at the point ν makes to the *sum for* γ^{-1} in (2.4). This fact greatly simplifies the expression obtained when we sum (2.8) over all possible values of l_ν : We also explicitly make use of the fact that we are restricting ourselves to systems where

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[2] Note that no factor $(k + 1)$ appears in this formula, because the definition (2.5) contains $k!$, *not* $(k + 1)!$.

the sum (2.4) converges after a finite number of terms even as $N \to \infty$. In this case we can omit the restriction $\sum(l_\nu + 1) \lesseqgtr N$ and the summation over the l_ν-values for the k particles 2, 3, $\cdots$, $k + 1$ are independent of each other. As mentioned before, the summation over all l_ν for each of the k factors in (2.8) separately simply gives one power of γ^{-1} for each of the k particles at which cluster diagrams can be attached. These factors then cancel the term γ^k which appears explicitly in (2.8) and we get our required expansion for $1/\gamma$ by summing over all values of k,

$$\gamma^{-1} = \sum_{k=0}^{\infty} \beta_k{}' \rho^k. \tag{2.9}$$

For k finite and N, $V \to \infty$ the cluster integrals $\beta_k{}'(T)$ in (2.9) are independent of V and therefore of density ρ and (2.9), if it converges, is a pure Taylor expansion for γ^{-1} in powers of ρ. One can also obtain an expansion in powers of ρ for $\ln \gamma$ which involves as coefficients the "simple irreducible cluster integrals" β_k, Eq. (2.5), which are somewhat simpler expressions than the $\beta_k{}'$: As indicated in (2.7), the coefficients β' can be expressed as sums of products of various β_k. Instead of evaluating the general expression for $\beta_k{}'$ in terms of the β, we shall derive the desired expression for $\ln \gamma$ by first regrouping the terms in (2.9) (or, rather, the corresponding cluster diagrams). Any "general 1-irreducible cluster diagram" with K points plus point 1 can be split into a unique number n of "simple irreducible" clusters by "snipping" only at the point 1. If $(k_\nu + 1)$ is the number of points in the νth of these n "simple irreducible" clusters, then $K = \sum_{\nu=1}^{n} k_\nu$. Apart from the single term $\beta_0{}' = 1$, we have $k_\nu \gtreqless 1$ and $n \gtreqless 1$. We now consider all the "general 1-irreducible" clusters with a fixed value of n but any value of K. If the ordering of the n clusters mattered then the expression $\prod_{\nu=1}^{n} \beta_{k_\nu} \rho^{k_\nu}$ would be a typical term in (2.9) and each k_ν could take on any integral value from unity to infinity.If we sum this expression over all k_ν, independently for each ν, we actually get $n!$ times the corresponding contributions to (2.9), since a diagram obtained merely by interchanging any of the n clusters is in fact not counted as a separate diagram. This factor $n!$ also appears in the few examples given in (2.7). Finally, summing over all $n \gtreqless 1$ and adding the term $\beta_0{}' = 1$, we obtain the desired result

$$\gamma^{-1} = 1 + \sum_{n=1}^{\infty} \frac{1}{n!} \left(\sum_{k=1}^{\infty} \beta_k \rho^k \right)^n = \exp\left(\sum_{k=1}^{\infty} \beta_k \rho^k \right), \qquad \ln \gamma = -\sum_{k=1}^{\infty} \beta_k \rho^k. \tag{2.10}$$

3. CLUSTER EXPANSION FOR THE TWO-BODY CORRELATION FUNCTION

We wish to derive next the well-known (see Ref. *3*, also *11*) expansion in powers of the density for the two-body correlation function $F_2(1,2)$. This quantity is a function of relative distance r_{12} only in our approximation of N^{-1}, $V^{-1} \to 0$ and is defined by Eq. (1.6),