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GENERALIZED CLUSTER EXPANSION
FOR REAL FLUIDS

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ABSTRACT

The equation of state and the pair correlation function of a real fluid is expressed in terms of the equation of state and distribution functions of a reference system. The derived general expression makes possible to obtain power series for the equation of state both in powers of a "softness" parameter ξ measuring the "amplitude" of the Boltzmann-factor difference, or in powers of a formal parameter λ measuring the "amplitude" of the potential difference (high temperature expansion).

АННОТАЦИЯ

Уравнение состояния и парная корреляционная функция реальной жидкости определяются с помощью уравнения состояния и корреляционных функций системы, выбранной в качестве референции. Полученное общее выражение позволяет выразить уравнение состояния в виде степенного ряда как по "параметру мягкости" ξ , измеряющему "амплитуду" разности больцмановских факторов, так и по параметру λ , измеряющему "амплитуду" разности потенциалов (высокотемпературное разложение).

KIVONAT

Egy reális folyadék állapotegyenletét és párkorrelációs függvényét kifejeztük egy referencia-rendszer állapotegyenlete és eloszlásfüggvényei segítségével. A levezetett általános kifejezésből az állapotegyenlet előálitható mind egy ξ "lágysági paraméter" (amely a Boltzmann-faktorok "amplitudóját" méri) hatványai szerint haladó, mind egy formális λ paraméter (amely a potenciálkülönbség "amplitudóját" méri) hatványai szerint haladó hatványsor alakjában (ez utóbbi a magas hőmérsékleti sorfejtés).

Recently a new perturbational method has been developed for the description of the equation of state and the pair correlation function for classical fluids¹. The method was successfully applied for a hard sphere reference system². This method contains an approximation concerning the calculation of certain cluster integrals. In this paper we derive general expressions for the equation of state and the pair correlation function for real fluids using the equation of state and distribution functions of a reference system in terms of diagrammatic expansion technique. We will show the connection between these generally derived expressions and those obtained in Ref. 1. We use the diagrammatic expansion technique developed by Morita and Hiroike³ and others^{4,5}. The notations and definitions are the same as those in Ref. 6.

Consider a homogeneous system with identical classical particles, where the interaction energy is the sum of pair interactions. Thus the grand partition function of the system can be written as

$$\begin{aligned} \Xi &= \sum_{N=0}^{\infty} \frac{1}{N!} \int \dots \int \prod_{i=1}^N z(\underline{r}_i) \prod_{i<j}^N e(\underline{r}_{ij}) d\underline{r}_1 \dots d\underline{r}_N = \\ &= \sum_{N=0}^{\infty} \frac{1}{N!} \int \dots \int \prod_{i=1}^N z(\underline{r}_i) \left[\prod_{i<j}^N f(\underline{r}_{ij}) d\underline{r}_1 \dots d\underline{r}_N \right] \end{aligned} \quad (1)$$

where $\underline{r}_{ij} = \underline{r}_i - \underline{r}_j$, and $z(\underline{r}_i) = z$ stands for the activity, which does not depend on \underline{r}_i for a uniform system. The Boltzmann-function and the Mayer-function are denoted by $e(r)$ and $f(r)$ respectively. The logarithm of Ξ can easily be expressed

in diagrammatic terms⁶ as

$\ln \Xi =$ [the sum of all distinct connected diagrams
consisting of black z-circles and f-bonds]

$$= \bullet + \bullet \text{---} \bullet + \begin{array}{c} \bullet \\ \diagup \quad \diagdown \\ \bullet \quad \bullet \end{array} + \begin{array}{c} \bullet \\ \diagup \quad \diagdown \\ \bullet \text{---} \bullet \end{array} + \dots \quad (2)$$

The n-particle density is defined as

$$\rho_n(\underline{r}_1 \dots \underline{r}_n) = \frac{1}{\Xi} z(\underline{r}_1) \dots z(\underline{r}_n) \frac{\delta^{(n)}}{\delta z(\underline{r}_1) \dots \delta z(\underline{r}_n)} \Xi \quad (3a)$$

where $\frac{\delta}{\delta z(\underline{r}_1)}$ denotes functional differentiation with respect to $z(\underline{r}_1)$. Applying the generalization of Lemma 2. in Ref.6, the following result can be obtained:

$$\rho_n(\underline{r}_1 \dots \underline{r}_n) = [\text{the sum of all distinct connected diagrams consisting of } n \text{ white z-circles labelled } \underline{r}_1 \dots \underline{r}_n, \text{ black z-circles, e-bonds between each pair of white circles and some or no f-bonds between other circles}] \quad (3b)$$

Now let us introduce a reference system with the pair potential $u_o(r)$, the thermodynamic and structural properties of which are assumed to be known (hereafter the index "o" always refers to the reference system). Introducing the notation $\Delta f = e^{-\beta v(r)} - 1$ (where $v(r) = u(r) - u_o(r)$) we can formally rewrite f as

$$f = f_o + e_o \Delta f \quad (4)$$

Substituting this formula into Eq. 2, the following expression

can be obtained for the logarithm of Ξ :

$$\ln \Xi = \ln \Xi_0 + \sum_{n=2}^{\infty} \Gamma_n \quad (5)$$

where

Γ_n = [the sum of all distinct connected diagrams consisting of at least n black z -circles, n of those are connected (at least) to another by an $e_0 \Delta f$ -bond, and some or no f_0 -bonds] (6)

Comparing now the definitions of ρ_n^0 and Γ_n we can see that the two sets of diagrams are similar to each other. In order to derive an exact relation between them, first we introduce the definition of an n -pont "skeleton diagram" $\sigma_{n,\mu}$, which consists of n white z -circles labelled $\underline{x}_1 \dots \underline{x}_n$, each of them is connected (at least) to an other by Δf -bond, e.g.

$$\begin{aligned} \sigma_{2,1}^c &= \text{---} \text{---} \text{---} \quad \sigma_{3,1}^c = \text{---} \text{---} \text{---} \quad \sigma_{3,2}^c = \text{---} \text{---} \text{---} \\ \sigma_{4,1}^c \dots \sigma_{4,6}^c &= \text{---} \text{---} \text{---} \quad \dots \quad \text{---} \text{---} \text{---} \\ \sigma_{4,1}^{dc} &= \text{---} \text{---} \end{aligned}$$

where the "c" and "dc" superscripts refer to the fact that the diagram is connected or disconnected, respectively. In terms of these skeleton diagrams the definition of Γ_n can be rewritten as follows:

$$\Gamma_n = \sum_{\mu} \frac{1}{s_{n,\mu}} \int \sigma_{n,\mu}(\underline{x}^n) \tilde{\rho}_{n,\mu}(\underline{x}^n) d\underline{x}^n \quad (7)$$

where $S_{n,\mu}$ is the symmetry number of the diagram which can be obtained from $\sigma_{n,\mu}$ by changing the white circles to black ones, and

$\tilde{\rho}_{n,\mu}$ = [the sum of all distinct connected diagrams which consist of n white circles labelled $\underline{r}_1 \dots \underline{r}_n$, black z -circles, e_o -bonds between those white circles which are connected in the corresponding skeleton by Δf -bonds, and some or no f_o -bonds]

In other words, Γ_n can be obtained by attaching the white circles of $\sigma_{n,\mu}$ to the corresponding circles of $\tilde{\rho}_{n,\mu}$, integrate over the white circles and take into account only the topologically distinct diagrams. Since the number of the topologically equivalent diagrams is just given by $S_{n,\mu}$ defined above, Eq.7. follows directly from (6).

It is easy to show that if the skeleton diagram is connected, then

$$\tilde{\rho}_{n,\mu}^c(\underline{r}^n) = \rho_n^o(\underline{r}^n) \quad (8)$$

since the sum of all those diagrams of $\tilde{\rho}_{n,\mu}$ which differs from each other only in the number and positions of the f_o -bonds between the white circles, results in a diagram which contains e_o -bonds between each pair of white circles, i.e. we get back the definition of ρ_n^o . If the skeleton is disconnected, the situation is more complicated. Assume now that $\sigma_{n,\mu}^{dc}$ splits into m subdiagrams (clusters) consisting of

n_1, n_2, \dots, n_m white circles labelled $\underline{r}^{n_1}, \underline{r}^{n_2} \dots \underline{r}^{n_m}$. If we carry out the summation of the diagrams in $\tilde{\rho}_{n,\mu}^{dc}$ similarly to that as in the case of $\tilde{\rho}_{n,\mu}^c$, we obtain

$\tilde{\rho}_{n,\mu}^{dc}$ = [the sum of all distinct connected diagrams consisting of n white z -circles labelled $\underline{r}_1 \dots \underline{r}_n$, black z -circles, e_o -bonds between each pair of white circles which are in the same cluster, and some or no f_o -bonds]

It is easy to show that the n -particle distribution function $\rho_n^o(\underline{r}^n)$ can be expressed in terms of the $\tilde{\rho}_{n,\mu}^{dc}$ functions which we call as "cluster distribution functions" in the following way. Assume that $n_1 \leq n_2 \leq \dots \leq n_m$ and construct a set of different $v_1, v_2 \dots v_M = n$ numbers by grouping the clusters containing $n_1, n_2 \dots$ atoms in each possible way:

$$\begin{aligned} v_1 &= n_1 \\ \vdots \\ v_M &= n_1 + n_2 + \dots + n_m = n \end{aligned}$$

Then

$$\begin{aligned} \rho_{v_1}^o &= \tilde{\rho}_{v_1}^o \\ \vdots \\ \rho_n^o &= \sum \tilde{\rho}_{v_1}^o \dots \tilde{\rho}_{v_2}^o \dots \end{aligned} \quad (9)$$

where the summation in the last equation extends, first, over all possible different combinations of the $v_1, v_2 \dots$ numbers for which $\sum v_i = n$, and second, for a given $\bar{v}_1, \bar{v}_2 \dots$ combination over all possible ways in which the coordinates $\underline{r}^{n_1}, \underline{r}^{n_2} \dots$ can be divided into groups consisting of $\bar{v}_1, \bar{v}_2 \dots$ atoms. The eqs. (9) follow directly from the fact that $\tilde{\rho}_v^o$'s

contain only connected diagrams while in the definition of ρ_v^0 '-s there are disconnected diagrams as well. The set of diagrams which represents $\tilde{\rho}_n^0$ obviously contains all connected diagrams of ρ_n^0 ($\tilde{\rho}_n^0$ is the connected part of ρ_n^0), while the disconnected parts can be written as different products of lower order (connected) cluster distribution functions. Thus the sum in eq. (9) will always contain the n-th order cluster distribution function $\tilde{\rho}_n^0$ and the different products of lower order $\tilde{\rho}_v^0$ '-s, and therefore

$$\tilde{\rho}_n^0 = \rho_n^0 - \sum'_{v_1 v_2} \tilde{\rho}_{v_1}^0 \dots \tilde{\rho}_{v_2}^0 \dots$$

where the prime denotes that $\tilde{\rho}_n^0$ is excluded from the summation. It is easy to show that $\tilde{\rho}_n^0$ defined in this way has the property, that it vanishes if the distance between the coordinates of one of the clusters (or any combinations of them) and the rest of the coordinates is large enough. We will show this by induction similarly to the case of the usual cluster functions⁷. Assume that this is true for $\tilde{\rho}_{v_1}^0 \dots \tilde{\rho}_{v_K}^0$ and consider $\tilde{\rho}_{v_{K+1}}^0 = \tilde{\rho}_v^0$. If the coordinates \underline{r}^v are divided into two groups, say $\underline{r}^{\bar{v}}$ and $\underline{r}^{v-\bar{v}}$ and the distance between these groups is large, then

$$\rho_v^0(\underline{r}^v) = \rho_{\bar{v}}^0(\underline{r}^{\bar{v}}) \rho_{v-\bar{v}}^0(\underline{r}^{v-\bar{v}})$$

and from (9) we obtain

$$\tilde{\rho}_v^0 + \sum'_{\Sigma v_i = v} \tilde{\rho}_{v_1}^0 \dots \tilde{\rho}_{v_2}^0 \dots = [\tilde{\rho}_{\bar{v}}^0 + \sum'_{\Sigma v_i = \bar{v}} \tilde{\rho}_{v_1}^0 \dots \tilde{\rho}_{v_2}^0 \dots] [\tilde{\rho}_{v-\bar{v}}^0 + \sum'_{\Sigma v_i = v-\bar{v}} \tilde{\rho}_{v_1}^0 \dots \tilde{\rho}_{v_2}^0 \dots]$$

According to our assumption the sum in the left-hand side of Eq. (10) contains only those terms which correspond to the given separation of the coordinates, because $\tilde{\rho}_{v_i}^o(\underline{r}^{v_i})=0$ if the coordinates \underline{r}^{v_i} are taken both from $\underline{r}^{\bar{v}}$'s and from $\underline{r}^{v-\bar{v}}$'s. Therefore this sum is just equal to the right-hand side of Eq. (10), that is

$$\tilde{\rho}_v^o = 0$$

This is also true for the lowest order non-trivial case, when

$$\tilde{\rho}_{n_1+n_2}^o = \rho_{n_1+n_2}^o - \rho_{n_1}^o \rho_{n_2}^o$$

This property assures the convergency of the expansion in eq. (7) in the thermodynamic limit, since in this case each term of the expansion is proportional to the volume V of the system, as can be seen very easily. Namely, if once the coordinates of one of the particles have been fixed, the region of integration (where the integrand differs from zero) is reduced to a finite volume determined by the range of interaction of the potential difference $v(r)$ inside a given cluster (when $\Delta f \neq 0$) while the convergency of the integration over the relative coordinates of the particles in different clusters is assured by $\tilde{\rho}(\underline{r}^n)$ which tends to zero for large distances.

Introducing now the notations

$$\begin{aligned} \beta_{VP_n}^c &= \sum_{\mu} \frac{1}{S_{n,\mu}} \int \sigma_{n,\mu}^c(\underline{r}^n) \rho_n^o(\underline{r}^n) d\underline{r}^n \\ \beta_{VP_n}^{dc} &= \sum_{\mu} \frac{1}{S_{n,\mu}} \int \sigma_{n,\mu}^{dc}(\underline{r}^n) \tilde{\rho}_{n,\mu}^o(\underline{r}^n) d\underline{r}^n \end{aligned} \quad (11)$$

and from (5) and (7) we obtain

$$\ln \Xi = \ln \Xi_0 + \beta V \sum_n (P_n^c + P_n^{dc})$$

or the equation of state

$$P = P_0 + \sum_n (P_n^c + P_n^{dc}) \quad (12)$$

Since the integrals in (11) are proportional to V , the quantities P_n^c and P_n^{dc} remains finite in the thermodynamic limit.

If the reference system is an ideal gas, then $\rho_n^0(\underline{r}^n) = z^n = \rho_0^n$ where ρ_0 stands for the density of the ideal gas reference system. It is easy to show from the definition (9) that in this case $\tilde{\rho}_{n,\mu}^0 = 0$ for all n and μ , and $\beta P_0 = \rho_0$. Thus

$$\beta P_n^c = \rho_0^n b_n$$

$$\beta P_n^{dc} = 0$$

where b_n 's are the reducible group integrals appearing in the usual activity expansion of the virial series and we obtain the well known result

$$\beta P = \rho_0 + \sum_{n=2}^{\infty} \rho_0^n b_n$$

The particle density can be calculated in the following way¹:

$$\rho = \rho_0 \left[1 + \left(\frac{\partial P_0}{\partial \rho_0} \right)^{-1} \sum_{n=2}^{\infty} \frac{\partial}{\partial \rho_0} (P_n^c + P_n^{dc}) \right] \quad (13)$$

The basic equations of the method are (12) and (13), which differ from those given in Ref. 1 in the presence of the corrections P_n^{dc} . These corrections contain, even in lowest order

two Δf -bonds. Introducing a "softness parameter" ξ , which is formally defined as

$$\overline{\xi \Delta f(r)} = \Delta f(r)$$

we can see that the contribution of the disconnected diagrams is of the order of ξ^2 . Since the results for the hard sphere reference system² show that in most of the cases the accuracy of the method is satisfactory already in first order, when only connected diagrams appear in the calculation, in applications the disconnected terms P_n^{dc} are of little importance.

Furthermore, we mention that expanding Δf in powers of the potential difference $v(r)$ and collecting the terms of the same order, Eqs. (12) and (13) allow us to calculate any higher order term in the high temperature expansion (or λ -expansion) as well (see e.g. in Ref.6.).

It is easy to calculate the pair correlation function $g_2(r)$ using Eq. (3) first order in ξ in the same way as in Ref. 1.:

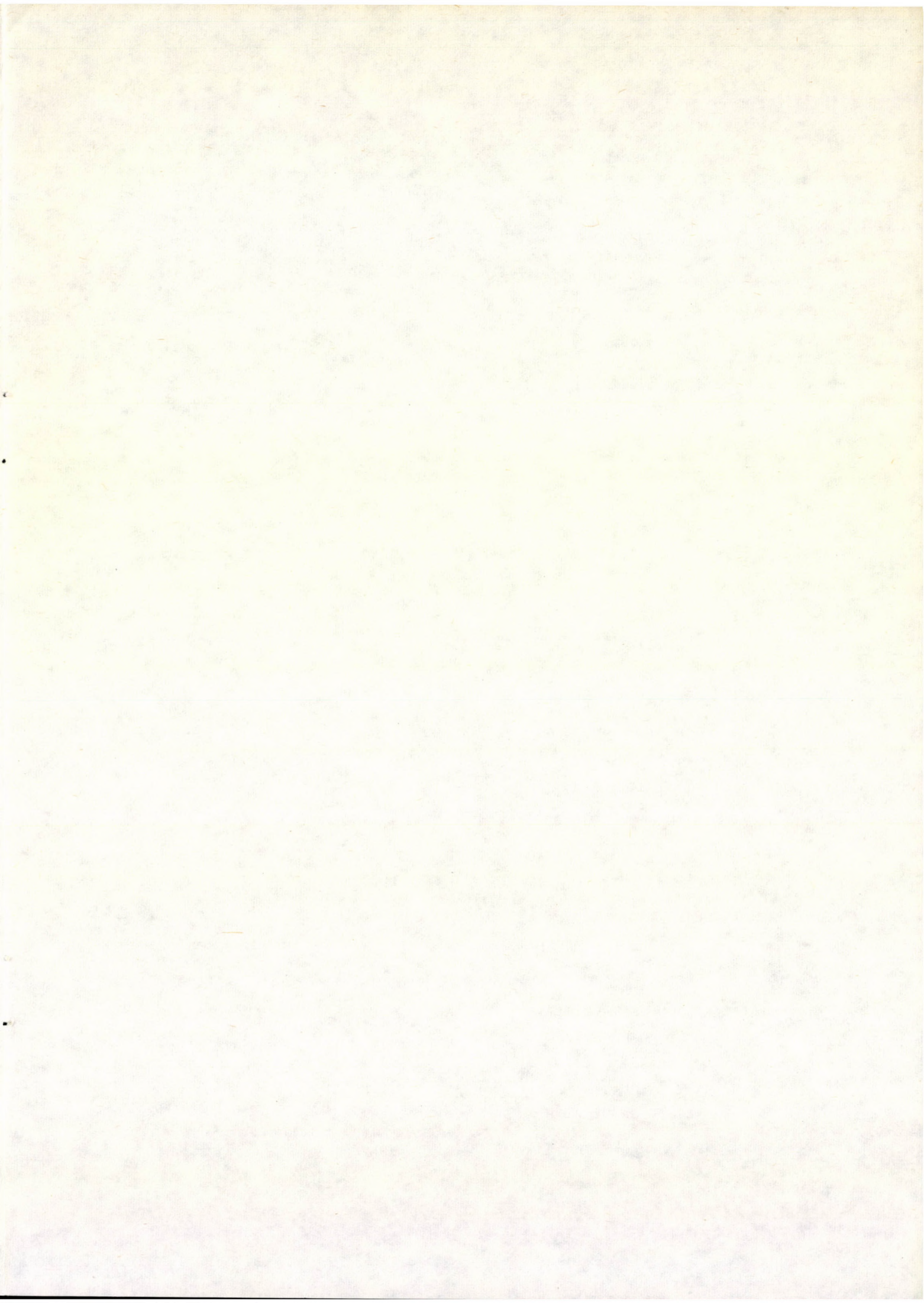
$$\begin{aligned} g_2(\underline{r}_{12}) &= g_2^0(\underline{r}_{12}) e^{-1}(\underline{r}_{12}) e(\underline{r}_{12}) + \xi 2\rho \int g_3^0(\underline{r}_1 \underline{r}_2 \underline{r}_3) \overline{\Delta f}(\underline{r}_{12}) d\underline{r}_3 \\ &\quad - \xi \frac{\partial P_2^c}{\partial \rho} \left(\rho \frac{\partial P_0}{\partial \rho} \right)^{-1} \left[\rho^2 g_2^0(\underline{r}_{12}) \right]' \\ &\quad + \xi \rho^2 \int [g_4^0(\underline{r}_1 \underline{r}_2 \underline{r}_3 \underline{r}_4) - g_2^0(\underline{r}_1 \underline{r}_2) g_2^0(\underline{r}_3 \underline{r}_4)] \overline{\Delta f}(\underline{r}_{34}) d\underline{r}_3 d\underline{r}_4 + O(\xi)^2 \end{aligned} \quad (14)$$

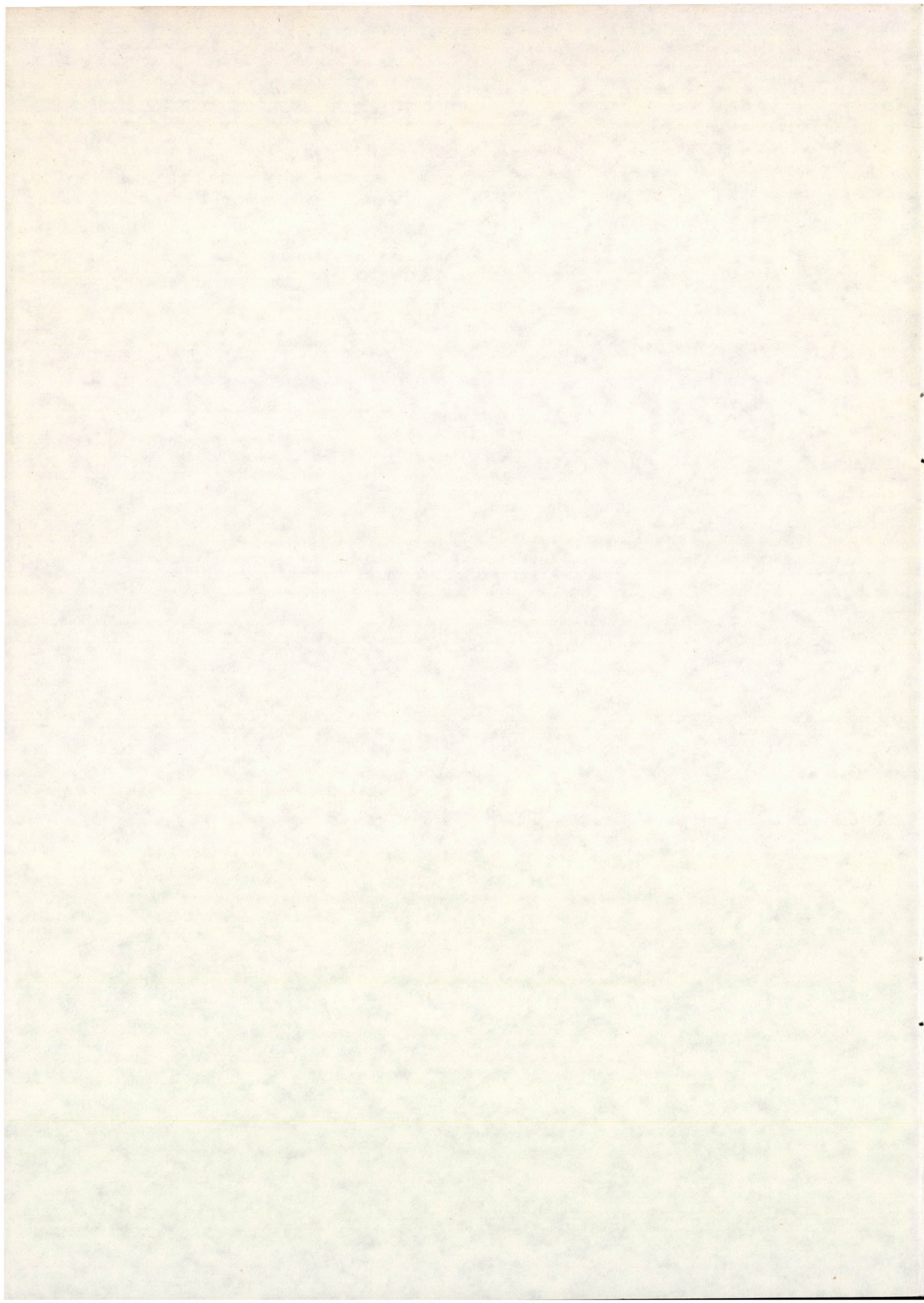
The last term in the right-hand side of (14) is the first order correction to the Eq. (23) of Ref. 1. This pair correlation function satisfies the compressibility equation and goes to unity for large distances as well.

To summarize we can say that we derived an exact expression for the equation of state ((12) and (13)) and the pair correlation function (Eq. (14)) of a real fluid using the equation of state and the distribution functions of a reference system and the $\Delta f(r)$ Mayer-function for the potential difference. From the general formulas one can derive power series for the equation of state both in powers of a softness parameter ξ or in powers of a formal parameter λ (high temperature expansion).

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