VIRIAL EXPANSION FOR NON-IDEAL REFERENCE SYSTEM
II. COMPARISON WITH PERTURBATION THEORY

By A. Fuliński

Department of Theoretical Chemistry, Institute of Chemistry, Jagellonian University, Cracov*

The renormalized virial expansion formulated in the first part of this work (preceeding paper) is used for the derivation of the perturbation expansion of the Helmholtz free energy, and of the s-particle distribution and correlation functions, around the known properties of the non-ideal reference system. The obtained results differ from those given earlier by Zwanzig from the direct perturbation expansion of the configurational integral. This discrepancy seems to be connected with the different order of various formal procedures, like the rearrangements of infinite series involved, and the limiting procedures, in both methods. It is suggested that the Zwanzig perturbation theory is connected rather with the cluster than with the virial expansion.

1. Introduction

In the first part of this work [1] (henceforth referred to as I) we have formulated the renormalization of the Ursell-Mayer virial expansion [2] of the Helmholtz free energy A, and of the s-particle distribution functions n_s (as well as of other functions connected with n_s), for the non-ideal reference system. It seems that the recent most promising approaches to the formulation of the adequate theory of liquids are those which make use of the known properties of some reference system with simplified interparticle interactions (usually a hard-core one). The best-known of these is the perturbation theory by Zwanzig [3] and Barker and Henderson [4] (*cf.* I for further references), and we wish in this part to compare our results with the results of the perturbation theory. However, the perturbation theory (as well as other theories of this kind — *cf.* I) has been so far constructed for the thermodynamic properties (free energy, equation of state) only, leaving aside the problem of calculation of the distribution functions. The knowledge of the free energy, as the function of the temperature T, and the volume per particle v, is sufficient for the complete thermodynamic (macroscopic) description of a fluid. More detailed information concerning also some details about the internal structure of the system, may be obtained from the know-

---

* Address: Zakład Chemii Teoretycznej, Instytut Chemii, Uniwersytet Jagielloński, Kraków, Krupnicza 41, Poland.

564

ledge of the (lower) s-particle distribution functions. Of special importance is the radial distribution function $g(r)$, which describes the probability of finding a particle at the distance r from a given particle, and which is directly measurable (*cf. e.g.* [5, 6]). When the total potential energy of the system is pair-additive, $g(r)$ contains also all the thermodynamical information about the system [5], and several approximate theories of fluids are formulated through integral equations for $g(r)$ [5–10]. We are thus also going to formulate in this part of the present work the analogon of the Zwanzig perturbation expansion for the radial distribution function and for other s-particle distribution functions.

We shall consider the same system as in I, with the same splitting of the potential energy, and of the Mayer functions, into the part describing the reference system, and the remainder. All the notations are also identical as in I; especially, the superscript or subscript 0 denotes the quantities describing the reference system. We shall only get rid — at the beginning — of the thermodynamical limit (I.2.1), because the perturbation theory of Zwanzig [3] does not make use of it.

2. Free energy

The canonical free energy of N-particle system, A_N, is given by (A_{id} is that from (I.2.3)):

$$e^{-(A_N - NA_{id})/kT} = Q_N = \frac{1}{N!} \int_V \cdots \int dr_1 \ldots dr_N e^{-\varphi_N(r^N)/kT}. \tag{2.1}$$

Write

$$\varphi_N(r^N) = \varphi_N^0(r^N) + \sum_{i>j=1}^{N} W(r_{ij}). \tag{2.2}$$

Here $\varphi_N(r^N)$ and $\varphi_N^0(r^N)$ are the total potential energies of the real (considered) and reference systems, and $W(r_{ij})$ is the same as in (I.3.1). $\varphi_N^0(r^N)$ may be eventually written as the sum of pair potentials $V^0(r_{ij})$; however, this is presently not necessary. In the Zwanzig perturbation theory [3], $\exp\{-\sum W(r_{ij})/kT\}$ in (2.1) is expanded into powers of $W(r_{ij})/kT$, and the so-obtained expansion of Q_N is rearranged further into the power series in $(1/T)$ of A_N:

$$A_N = A_N^0 + \sum_{n=1}^{\infty} \frac{\omega_n}{n!} \left(-\frac{1}{kT}\right)^{n-1} \tag{2.3}$$

(A_N^0 denotes the canonical free energy of the N-particle reference system).

The general expression for the n-th coeffcient ω_n is rather complicated; the first two coefficients are[1]:

$$\omega_1 = \tfrac{1}{2} \int dr_1 \int dr_2 W(r_{12}) n_2^0(12), \tag{2.4}$$

---

[1] Zwanzig [3] uses differently defined distribution functions: $P_s^0(r) = \dfrac{N!}{(N-s)!} n_s^0(r^s)$.

$$\omega_2 = \tfrac{1}{4} \int dr_1 \cdots \int dr_4 W(r_{12})W(r_{34})[n_4^0(1234) - n_2^0(12)n_2^0(34)] +$$

$$+ \int dr_1 \ldots \int dr_3 W(r_{12})W(r_{23})n_3^0(123) +$$

$$+ \tfrac{1}{2} \int dr_1 \int dr_2 [W(r_{12})]^2 n_2^0(12). \tag{2.5}$$

Let us now write $\exp\{-\sum W(r_{ij})/kT\}$ in terms of Mayer functions:

$$\exp\{-\sum W(r_{ij})/kT\} = \prod_{i>j=1}^{N} (1 + f_{ij}^1), \tag{2.6}$$

introduce the "coupling constant" γ $(\gamma = 1)$, multiply every Mayer function f^1 by this constant, and collect terms according to the power in γ:

$$\prod_{i>j=1}^{N} (1 + \gamma f_{ij}^1) = 1 + \gamma \binom{N}{2} f_{12}^1 + \gamma^2 \left[3 \binom{N}{3} f_{12}^1 f_{23}^1 + 3 \binom{N}{4} f_{12}^1 f_{34}^1 \right] +$$

$$+ \gamma^3 \left[\binom{N}{3} f_{12}^1 f_{23}^1 f_{31}^1 + 4 \binom{N}{4} f_{12}^1 f_{13}^1 f_{14}^1 + 12 \binom{N}{4} f_{12}^1 f_{23}^1 f_{34}^1 + \right.$$

$$\left. + 30 \binom{N}{5} f_{12}^1 f_{23}^1 f_{45}^1 + 15 \binom{N}{6} f_{12}^1 f_{34}^1 f_{56}^1 \right] + \ldots \tag{2.7}$$

Inserting (2.7) into (2.1), and making use of the definition (I.2.6) of the s-particle distribution function[2], we obtain the desired expansion of the configurational integral Q_N. Further rearrangement leads to the expansion of the free energy in powers of γ:

$$A_N = A_N^0 - kT \sum_{n=1}^{\infty} \frac{\gamma^n}{n!} \lambda_n(N, V, T), \tag{2.8}$$

$$\lambda_1 = \tfrac{1}{2} \int dr_1 \int dr_2 f_{12}^1 n_2^0(12), \tag{2.9}$$

$$\lambda_2 = \tfrac{1}{4} \int dr_1 \ldots \int dr_4 f_{12}^1 f_{34}^1 [n_4^0(1234) - n_2^0(12)n_2^0(34)] +$$

$$+ \int dr_1 \ldots \int dr_3 f_{12}^1 f_{23}^1 n^0(123), \tag{2.10}$$

$$\lambda_3 = \int dr_1 \ldots \int dr_3 f_{12}^1 f_{23}^1 f_{31}^1 n^0(123) +$$

$$+ \int dr_1 \ldots \int dr_4 f_{12}^1 f_{23}^1 (f_{24}^1 + 3 f_{34}^1) n^0(1234), \tag{2.11}$$

etc. Expanding the Mayer functions $f^1(r)$ into a power series of $W(r)/kT$, we rederive the Zwanzig results (2.3)–(2.5). The formula (2.8) forms thus a kind of perturbation series where the perturbation of the reference system is the Mayer function (= the renormalized potential) rather than the potential of interaction.

Further terms of the expansion (2.8) may be found (by means of formal rearrangements of the series, similar to that used by Zwanzig [3]), from the expansion (2.7); the latter may be defined in terms of the usual linear labeled graphs (not necessarily linked)

---

[2] s-particle distribution function $n_s^0(r^s)$ must be understood here as defined for the finite, N-particle system.

of the Ursell-Mayer theory [2].[3] This leads, however, to a quite complicated form, which will not be presented here.

We shall now rearrange the renormalized virial series of I to the form resembling (2.8). First, let us note that the Helmholtz free energy per particle, A, defined by (I.2.2), (I.3.4), (I.3.7) is related to A_N from (2.8) by (see *e.g.* [2]):

$$A(v, T) = \lim_{N \to \infty} \frac{1}{N} A_N(Nv, T) = \lim_{V \to \infty} \frac{v}{V} A_N(V, T), \qquad (2.12)$$

(where the limits are to be understood in the meaning of the thermodynamical limit (I.2.1)), so that, if we write

$$A = A_0 - kT \sum_{n=1}^{\infty} \frac{\gamma^n}{n!} \Lambda_n(v, T), \qquad (2.13)$$

we get

$$\Lambda_n(v, T) = \lim_{V \to \infty} \frac{v}{V} \lambda_n\left(\frac{V}{v}, V, T\right), \qquad (2.14)$$

if such a limit does exist, and if the order of the limiting procedure and of summation in (2.12) and (2.8) may be reversed.

The coefficients Λ_n may be determined from the renormalized virial expansion (I.3.7)–(I.3.10), collecting the terms according to the number of F^1-lines (*i.e.*, according to powers of the "coupling constant" γ). The result is:

$$\Lambda_n = \lim_{V \to \infty} \frac{1}{V} \sum_{m=M}^{2n} \left(\frac{1}{v}\right)^{m-1} \frac{n!}{m!} \int dr_1 \ldots \int dr_m \Lambda_n^m(r^m), \qquad (2.15)$$

$$\Lambda_n^m(r^m) = \sum_{[(\sigma_m)_n]} [N_m^0(r^m) - M_m^0(\sigma_m^n; r^m)] \prod_{(\sigma_m)_n} (F^1, F^0)_{ij}, \qquad (2.16)$$

where the graphs $(\sigma_m)_n$ are the reclassified graphs σ_m from I, containing m e-points and n F^1-lines; the remaining notation is the same as that in I (when a given graph $(\sigma_m)_n$ is double-linked, $M^0((\sigma_m)_n) = 0$). The lower limit M of the sum over m in (2.15) is to be determined from the relation[4,5]

$$1 + (8n+1)^{1/2} \leqslant 2M \leqslant 3 + (8n-7)^{1/2}. \qquad (2.17)$$

---

[3] *Cf.* also the next Section; the prescriptions for the graph representation of the expansion (2.7) are the same as those for the coefficients μ_n^s of the s-particle distribution function, with $s = 0$.

[4] The relation (2.17) follows from the fact that m points may be linked by at least $\binom{m-1}{2} + 1$ lines and at most by $\binom{m}{2}$ lines, when every point is to be linked with at least one other point, and when a given pair of points may be linked by at most one line.

[5] We list the first values of M for a given n: $n = 1$, $M = 2$; $n = 2-3$, $M = 3$; $n = 4-6$, $M = 4$; $n = 7-10$, $M = 5$; $n = 11-15$, $M = 6$; $n = 16-21$, $M = 7$; *etc.*

The first two coefficients are $(M_4^0(\alpha) - M_4^0(\delta)$ are given by (I.3.12)):

$$\Lambda_1 = -\frac{1}{v}D_2 = \frac{1}{2v}\int dr F^1(r) = \lim_{V\to\infty} \frac{v}{V}\frac{1}{2}\int dr_1 \int dr_2 f_{12}^1 n_2^0(12), \qquad (2.18)$$

$$\Lambda_2 = \lim_{V\to\infty}\frac{1}{V}\frac{1}{v^2}\int dr_1 \dots \int dr_3 F_{12}^1 F_{23}^1 [g_{31}^0 N_3^0(123)-1] +$$

$$+ \lim_{V\to\infty}\frac{1}{V}\frac{1}{4v^3}\int dr_1 \dots \int dr_4 F_{12}^1 F_{34}^1 \{N_4^0(1234)\,[F_{23}^0 F_{41}^0(2+4F_{13}^0 +$$

$$+ F_{13}^0 F_{24}^0)+1+4F_{23}^0(1+F_{24}^0)] - M_4^0(\alpha) - 4F_{23}^0 M_4^0(\gamma) -$$

$$- 4F_{23}^0 F_{24}^0 M_4^0(\delta)\} \qquad (2.19a)$$

$$= \lim_{V\to\infty}\frac{v}{V}\int dr_1 \dots \int dr_3 f_{12}^1 f_{23}^1 [n_3^0(123) - v n_2^0(12) n_2^0(23)] +$$

$$+ \lim_{V\to\infty}\frac{v}{V}\frac{1}{4}\int dr_1 \dots \int dr_4 f_{12}^1 f_{34}^1 \{[n_4^0(1234) - n_2^0(12) n_2^0(34)] -$$

$$- v n_2^0(34)\,[n_3^0(123) + v n_2^0(12) n_2^0(23) + n_2^0(12)\chi(1234)]\}, \qquad (2.19b)$$

$$\chi(1234) = \frac{1}{5v^2}\int dr_5 \left\{ [F_{15}^0 F_{25}^0 + H_3^0(125)]\,[F_{35}^0 F_{45}^0 + H_3^0(345)] - \right.$$

$$\left. - \frac{1}{6v}\int dr_6 F_{15}^0 F_{25}^0(2F_{56}^0 - f_{56}^0)F_{36}^0 F_{46}^0 \right\}. \qquad (2.19c)$$

Comparison of the above formula with that for λ_2, Eq. (2.10), shows that the relation (2.14) is not fulfilled, *i.e.*, that our renormalized virial expansion leads to results different from those obtained by the direct perturbation method of Zwanzig. The discussion of the possible explanation of this discrepancy is postponed to the last Section of this paper.

3. Distribution functions: direct perturbation

We shall write the definition (I.2.6) of the s-body distribution function $n_s(r^s)$ in the form (the thermodynamical limit is not used because we want to follow the Zwanzig formalism [3] of the perturbation theory):

$$n_s(r^s) = \frac{\lambda^{-3N}}{(N-s)!Z_0(N,V)} \frac{Z_0(N,V)}{Z(N,V)} \int dr_{s+1} \dots \int dr_N e^{-\varphi_N^0/kT} e^{-\varphi_N^1/kT}, \qquad (3.1)$$

with

$$Z_0(N,V) = \frac{\lambda^{-3N}}{N!}\int dr_1 \dots \int dr_N e^{-\varphi_N^0(r^N)/kT} \qquad (3.1a)$$

being the canonical partition function of the reference system. In analogy to Eqs (2.6) and (2.7), we write $\exp\{-\Phi_N^1/kT\}$ in terms of the Mayer functions f_{ij}^1 and the "coupling constant" γ; the difference here is that only particle indices from $s+1$ to N correspond to dummy integration variables in (3.1), and thus may be exchanged at will, whereas the indices from 1 to s must remain unchanged. We obtain:

$$e^{-\varphi^1{}_N(r^N)/kT} = e^{-\varphi^1{}_s(r^s)/kT} \prod_{i=1}^{s} \prod_{j=1}^{N} (1+f_{ij}^1) \prod_{l>k=s+1}^{N} (1+f_{kl}^1) =$$

$$= e^{-\varphi^1{}_s(r^s)/kT} \left\{ 1 + \gamma \left[\binom{N-s}{1} \sum_{i=1}^{s} f_{i,s+1}^1 + \binom{N-s}{2} f_{s+1,s+2}^1 \right] + \right.$$

$$+ \gamma^2 \left[\binom{N-s}{1} \sum_{j>i=1}^{s} f_{i,s+1}^1 f_{j,s+1}^1 + \binom{N-s}{2} \sum_{i=1}^{s} f_{i,s+1}^1 \sum_{j=1}^{s} f_{j,s+2}^1 + \right.$$

$$+ 2\binom{N-s}{2} f_{s+1,s+2}^1 \sum_{i=1}^{s} f_{i,s+1}^1 + 3\binom{N-s}{3} f_{s+1,s+2}^1 \sum_{i=1}^{s} f_{i,s+3}^1 +$$

$$\left. + 3\binom{N-s}{3} f_{s+1,s+2}^1 f_{s+2,s+3}^1 + 3\binom{N-s}{4} f_{s+1,s+2}^1 f_{s+3,s+4}^1 \right] +$$

$$+ \gamma^3 \left[\binom{N-s}{1} \sum_{k>j>i=1}^{s} f_{i,s+1}^1 f_{j,s+1}^1 f_{k,s+1}^1 + \binom{N-s}{2} \sum_{j>i=1}^{s} f_{i,s+1}^1 f_{j,s+1}^1 \times \right.$$

$$\times \sum_{k=1}^{s} f_{k,s+2}^1 + 2\binom{N-s}{2} f_{s+1,s+2}^1 \sum_{j>i=1}^{s} f_{i,s+1}^1 f_{j,s+1}^1 + \binom{N-s}{2} f_{s+1,s+2}^1 \times$$

$$\times \sum_{i=1}^{s} f_{i,s+1}^1 \sum_{k=1}^{s} f_{j,s+2}^1 + \binom{N-s}{3} \sum_{i=1}^{s} f_{i,s+1}^1 \sum_{j=1}^{s} f_{j,s+2}^1 \sum_{k=1}^{s} f_{k,s+3}^1 +$$

$$+ 2 \cdot 3 \binom{N-s}{3} f_{s+1,s+2}^1 f_{s+2,s+3}^1 \sum_{i=1}^{s} f_{i,s+1}^1 + 3\binom{N-s}{3} f_{s+1,s+2}^1 f_{s+2,s+3}^1 \times$$

$$\times \sum_{i=1}^{s} f_{i,s+2}^1 + \binom{N-s}{3} f_{s+1,s+2}^1 \sum_{j>i=1}^{s} f_{i,s+3}^1 f_{j,s+3}^1 + 2\binom{N-s}{3} f_{s+1,s+2}^1 \times$$

$$\times \sum_{i=1}^{s} f_{i,s+1}^1 \sum_{j=1}^{s} f_{j,s+3}^1 + \binom{N-s}{3} f_{s+1,s+2}^1 f_{s+2,s+3}^1 f_{s+3,s+1}^1 +$$

$$+4 \cdot 3 \binom{N-s}{4} f^1_{s+1,s+2} f^1_{s+3,s+4} \sum_{i=1}^{s} f^1_{i,s+1} + 3 \binom{N-s}{4} f^1_{s+1,s+2} f^1_{s+2,s+3} \times$$

$$\times \sum_{i=1}^{s} f^1_{i,s+4} + \binom{N-s}{4} f^1_{s+1,s+2} \sum_{i=1}^{s} f^1_{i,s+3} \sum_{j=1}^{s} f^1_{j,s+4} + 4 \binom{N-s}{4} f^1_{s+1,s+2} \times$$

$$\times f^1_{s+1,3s} + f^1_{s+1,s+4} + 12 \binom{N-s}{4} f^1_{s+1,s+2} f^1_{s+2,s+3} f^1_{s+3,s+4} +$$

$$+ 3 \binom{N-s}{5} f^1_{s+1,s+2} f^1_{s+3,s+4} \sum_{i=1}^{s} f^1_{i,s+5} + 30 \binom{N-s}{5} f^1_{s+1,s+2} f^1_{s+2,s+3} \times$$

$$\times f^1_{s+4,s+5} + 15 \binom{N-s}{6} f^1_{s+1,s+2} f^1_{s+3,s+4} f^1_{s+5,s+6} \Bigg] + O(\gamma^4) \Bigg\}, \tag{3.2}$$

where

$$\varphi^1_s(r^s) = \sum_{j>i=1}^{s} W(r_{ij}). \tag{3.3}$$

Inserting (3.2) into (3.1), we obtain the expansion of the s-particle distribution function in powers of γ:

$$n_s(r^s) = \frac{Z^0(N,V)}{Z(N,V)} e^{-\varphi^1{}_s(r^s)/kT} \left\{ n^0_s(r^s) + \sum_{n=1}^{\infty} \frac{\gamma^n}{n!} \mu^s_n(N,V,T;r^s) \right\}, \tag{3.4}$$

with

$$\mu^s_1 = \sum_{i=1}^{s} \int dr_{s+1} f^1_{i,s+1} n^0_{s+1}(r^{s+1}) + \tfrac{1}{2} \int dr_{s+1} \int dr_{s+2} f^1_{s+1,s+2} n^0_{s+2}(r^{s+2}), \tag{3.5}$$

$$\mu^s_2 = 2 \sum_{j>i=1}^{s} \int dr_{s+1} f^1_{i,s+1} f^1_{j,s+1} n^0_{s+1}(r^{s+1}) +$$

$$+ \int dr_{s+1} \int dr_{s+2} \Big[\sum_{i=1}^{s} f^1_{i,s+1} \sum_{j=1}^{s} f^1_{j,s+2} + 2 \sum_{i=1}^{s} f^1_{i,s+1} f^1_{s+1,s+2} \Big] n^0_{s+2}(r^{s+2}) +$$

$$+ \int dr_{s+1} \dots \int dr_{s+3} f^1_{s+1,s+2} \Big[\sum_{i=1}^{s} f^1_{i,s+3} + f^1_{s+2,s+3} \Big] n^0_{s+3}(r^{s+3}) +$$

$$+ \tfrac{1}{4} \int dr_{s+1} \dots \int dr_{s+4} f^1_{s+1,s+2} f^1_{s+3,s+4} n^0_{s+4}(r^{s+4}). \tag{3.6}$$

We do not write down the expression for μ^s_3, because it is lengthy, and may be easily found with the help of (3.2b), in analogy to the construction of μ^s_1 and μ^s_2. Higher-order coefficients

may be found by a diagrammatic technique similar to that of Ursell and Mayer [2]; the prescriptions for μ_n^s are:

(*i*) draw s root points, labeled from 1 to s;

(*ii*) draw k internal points ($M \leqslant k \leqslant 2n$), labeled from $s+1$ to $s+k$, M being the smallest number necessary to insert n lines, according to the prescription:

(*iii*) connect the points by n lines, in such a way that (a) every pair of points is connected by at most one line, (b) every internal point is connected with at least one other point, (c) root points are not connected directly with each other, and (d) root points may be not connected with any other point;

(*iv*) the contribution from a given diagram is obtained by writing the factor f_{ij}^1 for every line linking points labeled i and j, multiplying these factors by the function $(N-s-k)! n_{s+k}^0(r^{s+k})$, and integrating the resulting product over $r_{s+1} \ldots r_{s+k}$;

(*v*) μ_n^s is equal to the sum of contributions from all possible topologically different graphs built according to the above prescriptions, multiplied by $n!/(N-s)!$.

It is seen from the above that, in the n-th order perturbation, the s-particle distribution function is expressed through $s, s+1, \ldots s+2n$-particle distribution functions of the reference system.

Expansion (3.4) is not, however, the complete perturbation expansion of n_s, because of the presence of the complete partition function in the denominator. Note that

$$\frac{Z_0(N, V)}{Z(N, V)} = \frac{Q_N^0}{Q_N} = e^{-(A^0_N - A_N)/kT}, \tag{3.7}$$

so that, using the expansion (2.8), and expanding the resulting exponential function into a power series of γ (or using directly Eqs (2.1) and (2.7)), we obtain:

$$n_s(r^s) = e^{-\varphi^1_s(r^s)/kT} \left\{ n_s^0(r) + \sum_{n=1}^{\infty} \frac{\gamma^n}{n!} \lambda_n^s(N, V, T; r^s) \right\}, \tag{3.8}$$

with

$$\lambda_1^s = n_s^0(r^s) \cdot \frac{1}{2} \int dr_1 \int dr_2 f_{12}^1 n_2^0(12) + \mu_1^s, \tag{3.9}$$

$$\lambda_2^s = n_s^0(r^s) \cdot \left[\int dr_1 \ldots \int dr_3 f_{12}^1 f_{23}^1 n_3^0(123) + \frac{1}{4} \int dr_1 \ldots \int dr_4 f_{12}^1 f_{34}^1 n_4^0(r^4) \right] + $$
$$+ \mu_1^s \cdot \int dr_1 \int dr_2 f_{12}^1 n_2^0(12) + \mu_2^s, \tag{3.10}$$

etc. (the procedure is rather obvious). The exponent $\exp(-\varphi_s^1/kT)$ in (3.4) and (3.6) may also be expanded in powers of γ:

$$e^{-\varphi^1_s(r^s)/kT} = \prod_{j>i=1}^{s} (1 + f_{ij}^1) = 1 + \gamma \sum_{j>i=1}^{s} f_{ij}^1 + $$

$$+ \gamma^2 \left[\sum_{k>j>i=1}^{s} (f_{ij}^1 f_{ik}^1 + f_{ij}^1 f_{jk}^1 + f_{ik}^1 f_{jk}^1) + \right.$$

$$\left. + \sum_{j>i=1}^{s} f_{ij}^1 \sum_{l>k=1}^{s} {}' f_{kl}^1 \right] + O(\gamma^3), \tag{3.11}$$

where the primed sum in the last term of γ^2 means that in a given product $f_{ij}^1 f_{kl}^1$, the pair index kl must be different from the pair index ij. In the graph representation formulated above, the expression (3.11) is obtained by inserting — in all possible ways — the lines between root points.

The expansion (3.8) together with (3.11) is the most complete perturbation expansion in Mayer functions $f^1(r)$ (in powers of the "coupling constant" γ), whereas, for some practical purposes the form (3.8), or even the expansion (3.4) (without expanding $\exp(-\varphi_s^1/kT)$) may be more convenient. Let us note, however, that if we are interested in the expansion in powers of inverse temperature (Zwanzig perturbation expansion, which may be easily obtained from the above formulae by expanding Mayer functions into power series of W/kT), both expansions, (3.8) and (3.11), should be used. We do not write down explicitly such an expansion for $n_s(r^s)$, because it is rather obvious.

As we have mentioned, of special importance is the radial distribution function $g(r)$. Whereas the perturbation expansion of $g(r)$ in powers of Mayer functions is given by (3.4), (3.8), and (3.11), we present explicitly, for the sake of completeness, the Zwanzig perturbation expansion for $g(r)$:

$$g(r) = v^2 n_2(r) = g^0(r) + \sum_{n=1}^{\infty} \frac{\xi_n(r)}{n!}\left(-\frac{1}{kT}\right)^n, \tag{3.12}$$

$$\xi_1(r_{12}) = g^0(r_{12})\left[W(r_{12}) + \tfrac{1}{2}\int dr_3 \int dr_4 W(r_{34}) n_2^0(r_{34})\right] +$$
$$+ v^2 \int dr_3 [W(r_{13}) + W(r_{23})] n_3^0(123) + \tfrac{1}{2} v^2 \int dr_3 \int dr_4 W(r_{34}) n_4^0(1234), \tag{3.13}$$

$$\xi_2(r_{12}) = W^2(r_{12}) g^0(r_{12}) + v^2 \int dr_3 (W_{13} + W_{23})(W_{13} + W_{23} +$$
$$+ 2W_{12}) n_3^0(123) + v^2 \int dr_3 \int dr_4 \{W_{34}(W_{12} + \tfrac{1}{2} W_{34}) [n_4^0(r^4) +$$
$$+ n_2^0(12) n_2^0(34)] + (W_{13} + W_{23})(W_{14} + W_{24} + 2W_{34}) n_4^0(r^4)\} +$$
$$+ v^2 \int dr_3 \dots \int dr_5 W_{45} \{W_{34} n_2^0(12) n_3^0(345) + (W_{13} + W_{23}) n_2^0(45) n_3^0(123) +$$
$$+ (W_{13} + W_{23} + W_{34}) n_5^0(r^5)\} + \tfrac{1}{4} \int dr_3 \dots \int dr_6 W_{34} W_{56} [n_2^0(12) n_3^0(3456) +$$
$$+ 2n_2^0(56) n_4^0(1234) + n_6^0(r^6)]. \tag{3.14}$$

4. Distribution functions: perturbation from the virial expansion

In this Section we shall write down, for the sake of completeness, the perturbation expansion in powers of the "coupling constant" γ, the s-particle distribution $n_s(r^s)$, correlation $N_s(r^s)$ and $G_s(r^s)$, and pseudopotential $h_s(r^s)$ functions. Let us note that the perturbation expansions of N_s, G_s, and h_s are rather difficult to be obtained by the direct methods used (for n_s) in the preceeding Section. Although such a task is not impossible, it would require fairly complicated manipulations of products of sums and series representing different functions of distribution and correlation functions. It is simpler to rearrange

the virial expansions of I into corresponding perturbation expansions, collecting the terms according to the number of F^1-lines in the graphs representing the virial coefficients. We obtain, in analogy to (2.13)–(2.19):

$$n_s(r^s) = e^{-\varphi_s{}^1(r^s)/kT} n_s^0(r^s) \left\{ 1 + \sum_{n=1}^{\infty} \frac{\gamma^n}{n!} P_{s,n}(T, v; r^s) \right\},$$

$$N_s(r^s) = N_s^0(r^s) \left\{ 1 + \sum_{n=1}^{\infty} \frac{\gamma^n}{n!} Q_{s,n}(T, v; r^s) \right\},$$

$$G_s(r^s) = G_s^0(r^s) \left\{ 1 + \sum_{n=1}^{\infty} \frac{\gamma^n}{n!} R_{s,n}(T, v; r^s) \right\}, \tag{4.1}$$

$$h_s(r^s) = h_s^0(r^s) + \sum_{n=1}^{\infty} \frac{\gamma^n}{n!} S_{s,n}(T, v; r^s),$$

$$T_{s,n}(T, v; r^s) = \sum_{k=M}^{2n} v^{-k} \frac{n!}{k!} \frac{1}{N_s^0(r^s)} \int dr_{s+1} \cdots \int dr_{s+k} \times$$

$$\times \left\{ \sum_{[(a_k{}^s)_n]} \prod_{(a_k{}^s)_n} (F^1, F^0)_{ij} N_{k+s}^0(r^{k+s}) + \right.$$

$$\left. + \sum_{[(\alpha_k{}^s)_n]} [N_{k+s}^0(r^{k+s}) - A_{k+s}^0((\alpha_k^s)_n; r^{k+s})] \prod_{(\alpha_k{}^s)_n} (F^1, F^0)_{ij} \right\}, \tag{4.2}$$

where

$$T_{s,n} = P_{s,n}, Q_{s,n}, R_{s,n}, S_{s,n},$$

$$A_{k+s}^0 = I_{k+s}^0, J_{k+s}^0, K_{k+s}^0, L_{k+s}^0,$$

$$a_k^s = q_k^s, n_k^s, m_k^s, p_k^s,$$

$$\alpha_k^s = \omega_k^s, v_k^s, \mu_k^s, \pi_k^s,$$

for n_s, N_s, G_s, h_s, respectively, graph $(g_k^s)_n$ is the graph g_k^s, which contains n F^1-lines, M is the minimal number of internal points, which are necessary for a given graph with s root points to contain n F^1-lines, and the remaining notation is the same as in I. Again, the factor $\exp(-\varphi_s^1/kT)$ in n_s may be expanded further in powers of γ, and (4.2) may be expanded further in powers of $(-1/kT)$, in order to derive the temperature perturbation expansion.

The perturbation expansion (4.1), obtained from the renormalized virial expansion, provides, similarly as in the case of the free energy, results which differ from those (Eq.

(3.8)) obtained by the direct perturbation. As an example, we write down explicitly the first terms of the expansion of the radial distribution function (*cf.* Eqs (3.12)–(3.14), and (I.4.20)–(I.4.25)):

$$g(r_{12})_{vp} = g(r_{12})_{dp} - e^{-W(r_{12})/kT}\frac{1}{v}g^0(r_{12})\int dr_3(F_{13}^1 + F_{23}^1) -$$

$$- e^{-W(r_{12})/kT}g^0(r_{12})\frac{1}{2v^2}\int dr_3\int dr_4 F_{34}^1\{H_3^0(123) + H_3^0(124) +$$

$$+ g^0(r_{13})g^0(r_{14})\left[G_3^0(134) + F_{23}^0 N_4^0(1234)\right] + g^0(r_{23})g^0(r_{24}) \times$$

$$\times \left[G_3^0(234) + F_{13}^0 N_4^0(1234)\right] - \left[g^0(r_{13})g^0(r_{24}) - 1\right]N_4^0(1234)\} + O(\gamma^2), \tag{4.3}$$

where

$$g(r_{12})_{dp} = e^{-W(r_{12})/kT}\left\{g^0(r_{12}) + v^2\int dr_3(f_{13}^1 + f_{23}^1)n_3^0(123) +\right.$$

$$\left. + \frac{1}{2}\int dr_3\int dr_4 f_{34}^1\left[v^2 n_4^0(1234) + \frac{1}{v^2}g^0(r_{12})g^0(r_{34})\right] + O(\gamma^2)\right\}, \tag{4.4}$$

where the subscripts *vp*, *dp* mean "virial perturbation" (*i.e.*, perturbation expansion (4.11)), and "direct perturbation", Eq. (3.8), respectively.

5. Final remarks

The renormalized virial expansion obtained in I represents the subsequent virial coefficients of the Helmholtz free energy, and of *s*-particle distribution, correlation, and pseudopotential functions, in terms of the graphs, classified formally by the number of *e*-points and the topology with respect to F^1 and F^0-lines. This form resembles closely the original Ursell-Mayer virial expansion [2], the main differences being (*i*) in the presence of two different kinds of lines, which changes the topology and increases the number of different graphs (compare Figs 1 and 9 of I, for example), (*ii*) in the presence of some not double-linked graphs, and (*iii*) in the fact that the new virial coefficients depend on density through the density dependence of the correlation functions of the reference system. The latter disturbs the idea of the original virial expansion as the expansion in powers of the density of the system. However, because of the well-defined graphical representation of subsequent terms, the discussed form of the virial expansion permits one to handle formally the whole infinite series, enabling one, for example, to apply the techniques of partial summations (*e.g.*, ring approximation) of this series. Approximations of this kind will be discussed in subsequent parts of this work. In this respect the proposed formalism seems to be more flexible than the usual perturbation expansions.

The results obtained in this part show that the renormalized virial expansion, when rearranged into "perturbation" series, leads to expressions which are different from those given by the direct perturbation method of Zwanzig. Some explanation of this discrepancy

may be obtained by considering the limiting case when the reference system is that of the ideal gas, *i.e.*, when

$$V^0(r) = \varphi^0(r^N) = 0, \quad N_s^0 = g^0 = 1, \quad f^1(r) = F^1(r) = f(r),$$

$$F^0(r) = H_s^0(r^s) = 0. \tag{5.1}$$

In this case, both Eq. (2.9) and Eq. (2.18) give correctly the second virial coefficient of the free energy. However, the next terms are:

$$\Lambda_2 = 0, \quad \lambda_2 = \frac{1}{v^2} \frac{N}{V} \int dr_1 \dots \int dr_3 f_{12} f_{23} \neq 0, \tag{5.2}$$

Now, $\Lambda_2 = 0$ is in agreement with the results of the Ursell-Mayer virial expansion, which does not contain any term proportional to γ^2 (*i.e.*, given by an integral over two Mayer functions): after the second virial coefficient, the lowest term contains three Mayer functions (*cf.* Section 2 of I). On the other hand, a term of type of λ_2 from (5.2), which is described by a single-linked graph, is present in the cluster expansion, *i.e.*, in the expansion in powers of the fugacity (active density) [2]. A similar analysis may be performed for the expressions describing the distribution functions. It seems thus that the Zwanzig perturbation series is connected rather with the cluster than with the virial series of Ursell and Mayer, which, in turn, is probably connected with details of the limiting procedures leading from one series to the other [2], and mentioned in the relations (2.12) and (2.14).

REFERENCES

[1] A. Fuliński, *Acta Phys. Polon.*, **A41**, 419 (1971).
[2] G. E. Uhlenbeck, G. W. Ford, *Studies in Statistical Mechanics*, North-Holland Publ. Co., Amsterdam 1962, Vol. I, Part B.
[3] R. W. Zwanzig, *J. Chem. Phys.*, **22**, 1420 (1954).
[4] J. A. Barker, D. Henderson, *J. Chem. Phys.*, **47**, 2856 (1967).
[5] J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquids*, J. Wiley, New York 1954.
[6] G. H. A. Cole, *Phil. Mag. Supplement*, 8, 225 (1959).
[7] J. G. Kirkwood, M. B. Boggs, *J. Chem. Phys.*, 10, 394 (1942).
[8] J. K. Percus, G. J. Yevick, *Phys. Rev.*, 110, 1 (1958).
[9] J. M. J. Van Leeuwen, J. Groeneveld, J. De Boer, *Physica*, 25, 792 (1959); 30, 2265 (1969).
[10] T. Morita, *Progr. Theor. Phys.*, 41, 339 (1969).