# VIRIAL EXPANSION FOR NON-IDEAL REFERENCE SYSTEM I. GENERAL FORMULATION

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The Ursell-Mayer virial expansion of the Helmholtz free energy, and of the $s$-particle distribution and correlation functions is renormalized for a non-ideal reference system. The total potential energy of intermolecular interactions is split into two parts, that describing the interactions in the reference system, and the remainder. The concept of graphs composed of two kinds of lines (bicoloured lines), $F^0$-line representing the interactions of the reference system, and $F^1$-line representing the remainder interactions is introduced; the graphs describing the Ursell-Mayer virial expansion are regrouped and resummed into renormalized virial graphs classified according to the topology with respect to $F^1$-lines. The renormalized virial expansion enables the systematic introduction of the subsequent corrections from the true form of interaction to be made, as well as formal approximations (ring approximation, for example), into the known expressions describing the properties of the reference system, to be performed.

## *1. Introduction*

The early van der Waals idea of the separation of hard-core and attractive parts of the intermolecular potential has been revived recently in the more refined form of the perturbation theory of dense gases and liquids. In its original form, introduced first by Zwanzing [1], the perturbation theory, providing in fact the expansion in powers of inverse temperature, proved to be useful at high temperatures only [1–5]. A more suitable form of the perturbation equation of state was found by Barker, Henderson, and coworkers [6]; the second-order term of the perturbation expansion is approximated there on the basis of semimacroscopic arguments. The Barker-Henderson equation is applicable at quite low temperatures, as well as at densities close to the solid phase [6–9]. Mansoori and Canfield [9] applied the approximation introduced by Barker and Henderson to the third-order term, using at the same time the variational method for the calculation of the proper hard-core diameters. Their method describes the properties of liquid state,

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gaseous state, and the liquid-vapour phase transition; however, their calculations of the thermodynamic properties at the critical point lead to results [9] which are slightly worse than those obtained from the Barker-Henderson equation [6, 9].

It seems that, because of the rapidly growing complication of subsequent terms, the limits of the practical applicability of the perturbation methods have been approached in the abovementioned works, and that for further progress may be obtained by different methods; indeed, propositions other techniques based on the separation of intermolecular interactions into some simple reference system and the remaining part (not necessarily treated as perturbation) have been recently published (*cf. e. g.* [9–13]). In this work we want to propose still another method of this kind, by deriving the analogon of the well-known Ursell Mayer vir al expansion (*cf. e. g.* [14]), reformulated for an arbitrary non-ideal reference system. It will be shown how this renormalized virial expansion may serve as a suitable, well-defined basis for different kinds of approximations, both of the perturbation, and of the formal type, especially for the partial summations (ring or chain approximations, for example) of infinite series involved in the general theory. Such approximat ons will be dealt with in the subsequent parts of this work; in this part the general formulation will be presented.

## 2. *Graph formulation of the virial expansion*

In this Section we shall briefly sketch the main features of the graphical representation of the usual Ursell-Mayer virial expansion. The details collected here will be needed in the subsequent calculations, and it is perhaps better to present them in a systematic way. The following is taken mainly from Ref. [14], although there are some minor alterations in notation (mainly simplifying ones). Besides, a few additional (rather trivial) definitions (functions $N_s$ and $G_s$), which will be of some use below, are introduced.

Consider a system of $N$ identical particles contained in volume $V$, kept at temperature $T$, and interacting with each other through the pair potential $V(r)$. It is assumed that quantum effects are negligible, and the thermodynamic limit,

$$N \to \infty, \; V \to \infty, \; N/V = 1/v = \varrho = \text{finite}, \tag{2.1}$$

is considered.

We take as the starting point the Ursell-Mayer virial expansion [14] for the Helmholtz free energy[1] per one particle, $A$,

$$A = A_{id} + kT \sum_{m=2}^{\infty} C_m \left(\frac{1}{v}\right)^{m-1}, \tag{2.2}$$

[1] Usually one deals with the virial series for the pressure $p$: $\frac{p}{kT} = \frac{1}{v} + \sum_{2}^{\infty} B_m \, v^{-m}$; however, we prefer to consider here the free energy, which is a much more general function. The relations between both series are obvious: $p = -(\partial A/\partial v)_T$, which implies $C_m = B_m/(m-1)$.

where

$$A_{id} = -kT\{1+\ln(v/\lambda^3)\}, \quad \lambda = (2\pi\hbar^2/mkT)^{1/2}, \tag{2.3}$$

is the ideal gas contribution ($\hbar$ is Planck's constant, $m$ is the mass of the particle, $k$ is Boltzmann's constant).

The free energy virial coefficients $C_m$ are:

$$C_m = C_m(T) = -\lim_{V\to\infty} \frac{1}{V}\frac{1}{m!}\int_V \dots \int_V dr_1 \dots dr_m V_m(r^m),$$

$$V_m(r^m) = V_m(r_1, \dots, r_m) = \sum_{\{S_m\}} \prod_{S_m} f_{ij}, \tag{2.4}$$

$$f_{ij} = f(r_{ij}) = \exp\{-V(r_{ij})/kT\} - 1, \quad r_{ij} = |r_i - r_j|, \tag{2.5}$$

where the sum is taken over the finite set $\{S_m\}$ of all possible topologically different $m$-point labeled double-linked linear graphs, the contribution from the graph $S_m$ written in such a way that every line joining two points labeled $i$ and $j$ imparts a factor equal to the Mayer function $f_{ij}$ (for more details *cf.* Ref. [14]). As an example, all the graphs[2] representing $V_4$ are drawn in Fig. 1.

Besides the free energy, which contains all the thermodynamical information about the system, of interest for the theory of liquids are the $s$-particle distribution functions $n_s(r^s; T, v)$, which contain information concerning the microscopic structure of the system.

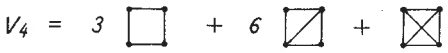


Fig. 1. Graph representation of the fourth virial coefficient. The numerical factors preceding graphs are the combinatorial factors expressing the number of topologically different possible labelings of the graphs

We shall thus discuss also these functions, the more that in the following calculations we shall need some details of the graphical representation of these functions. $n_s(r^s)$ is defined by [14]:

$$n_s(r^s) = \lim_{N\to\infty} \frac{\lambda^{-3N}}{(N-s)!Z(N, V)} \int dr_{s+1} \dots \int dr_N e^{-\varphi_N(r^N)/kT}, \tag{2.6}$$

where the limit is to be understood in the sense of (2.1). $\varphi_N$ is the total potential energy, and the canonical partition function $Z(N, V)$ is:

$$Z(N, V) = \frac{\lambda^{-3N}}{N!} \int dr_1 \dots \int dr_N e^{-\varphi_N(r^N)/kT} \tag{2.6a}$$

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[2] These are unlabeled graphs; the number of possible different labelings of the points (the so-called combinatorial factor) is written before each graph. Note that, after integrations required by (2.4), the contribution from a given graph does not depend on the labeling [14].

$n_s(\boldsymbol{r}^s)$ and the subsequently defined functions are symmetrical with respect to the exchange of the particle labels.

Of main importance for many applications is the radial distribution (correlation) function $g(r)$, defined by:

$$n_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = v^{-2}\, g(r_{12}) = v^{-2}\, e^{-V(r_{12})/kT} \overline{N}_2(r_{12}) \tag{2.7}$$

(for the angle-independent intermolecular potential $V(r)$, and for translationally invariant system, two-particle distribution depends only on the relative distance of particles). It is also convenient for further purposes to introduce the $s$-particle correlation functions $N_s(\boldsymbol{r}^s)$, $s$-particle reduced correlation functions $G_s(\boldsymbol{r}^s)$, and $s$-patricle effective pseudo-potentials $h_s(\boldsymbol{r}^s)$:

$$n_s(\boldsymbol{r}^s) = v^{-s}\Big[\prod_{\{i,j\} \subset \{s\}} g(r_{ij})\Big] \cdot N_s(\boldsymbol{r}^s), \qquad N_2(r_{ij}) = 1, \tag{2.8}$$

$$\left.\begin{aligned} N_s(\boldsymbol{r}^s) &= \prod_{\{l \geqslant 3\} \subset \{s\}} G_l(\boldsymbol{r}^l), \\ G_2(r_{ij}) &= g(r_{ij}), \qquad N_3(\boldsymbol{r}^3) = G_3(\boldsymbol{r}^3), \end{aligned}\right\} \tag{2.9}$$

$$G_s(\boldsymbol{r}^s) = \exp\,[h_s(\boldsymbol{r}^s)]. \tag{2.10}$$

The product in (2.9) is over all groups of $l \geqslant 3$ particles, which are the subsets of the set $\{s\}$.

The virial expansion of $n_s$ has the form:

$$n_s(\boldsymbol{r}^s; v) = v^{-s} \prod_{\{i,j\} \subset \{s\}} e^{-V(r_{ij})/kT}\Big[1 + \sum_{k=1}^{\infty} d_k^s(\boldsymbol{r}^s) v^{-k}\Big], \tag{2.11}$$

$$d_k^s(\boldsymbol{r}^s) = \frac{1}{k!} \int d\boldsymbol{r}_{s+1} \cdots \int d\boldsymbol{r}_{s+k} \sum_{\{Q_k^s\}} \prod_{Q_k^s} f_{ij}, \tag{2.12}$$

where the sum in (2.12) is over all topologically different linear graphs $Q_k^s$ built as follows: (*i*) the graph contains $s$ root points (labeled 1, ..., $s$, and corresponding to $\boldsymbol{r}^s$), and $k$ internal points (labeled $s+1$, ..., $s+k$, and corresponding to integration variables); (*ii*) points are joined by lines representing the Mayer functions $f_{ij}$; (*iii*) there are no direct lines between root points; (*iv*) when lines are inserted joining all the root points (in all possible ways), the graph becomes a double-linked graph (a star $S_{k+s}$). As an example, typical graphs representing $n_4$ are shown in Fig. 2A; Fig. 2B shows first graphs of the virial expansion of the radial distribution function.

Virial expansions of the functions $N_s$, $G_s$, and $h_s$ may also be formulated in terms of appropriate classes of graphs, due to the so-called product theorem [14]. The product theorem states that, if a given graph $Q_k^s$ may be made disjoint by cutting off all its root points, then the total contribution from this graph to $d_k^s(\boldsymbol{r}^s)$ (including integrations in (2.12)) is equal to the product of contributions from all its disjoint (in the above sense) parts,

when these are completed by adding (independently to every part) the lacking root points. The product theorem is illustrated in Fig. 2C. It is the product theorem, which enables us to write the definitions (2.8)–(2.10); owing to it, the fragments of the graphs $Q_k^s$, represent-

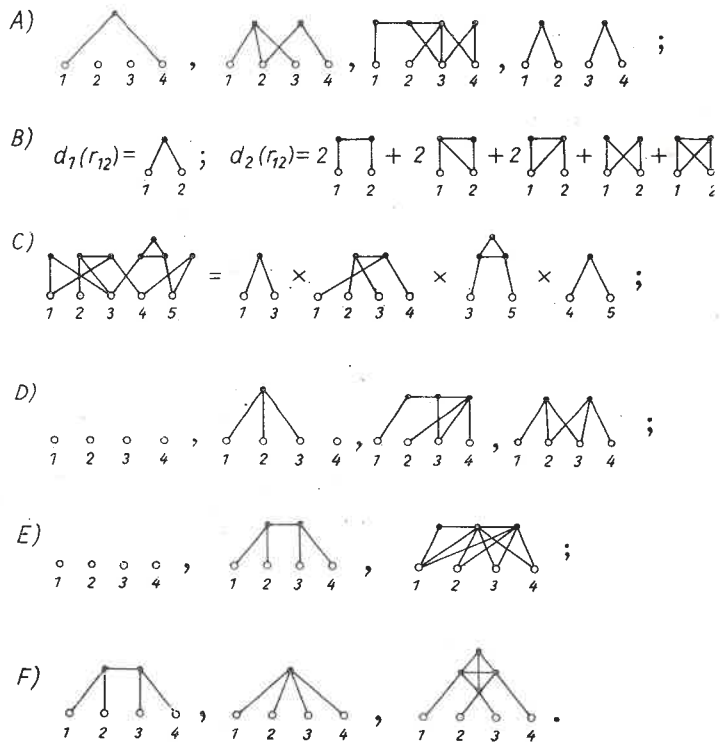


Fig. 2. Rooted graphs representing distribution functions: A) typical graphs representing $n_4$; B) first terms of the virial expansion of $g(r_{12})$ — combinatorial factors included; C) illustration of the product theorem; D)—F) typical graphs representing $N_4$, $G_4$, and $h_4$, respectively

ing the contributions to $g(r_{ij})$, and other fragments, may be separated out, and the graphical representation of the virial expansion of $N_s$, $G_s$, and $h_s$ may be found:

$$N_s(\boldsymbol{r}^s) = 1 + \sum_{k=1}^{\infty} a_k^s(\boldsymbol{r}^s) v^{-k}, \tag{2.13}$$

$$G_s(\boldsymbol{r}^s) = 1 + \sum_{k=1}^{\infty} b_k^s(\boldsymbol{r}^s) v^{-k}, \tag{2.14}$$

$$h_s(\boldsymbol{r}^s) = 1 + \sum_{k=1}^{\infty} c_k^s(\boldsymbol{r}^s) v^{-k}, \tag{2.15}$$

where $a_k^s$, $b_k^s$, $c_k^s$ are given by formulae analogous to (2.12), but with summations over the classes of graphs $\{N_k^s\}$, $\{M_k^s\}$, $\{P_k^s\}$, which are subclasses of $\{Q_k^s\}$, defined by:

a) in the graph $N_k^s$, every internal point is joined by an internal path (*i. e.*, by a se-

quence of lines, which does not pass through any root point) with at least three root points;

b) in the graph $M_k^s$, every internal point is joined by an internal path with every of the $s$ root points;

c) in the graph $P_k^s$, every pair of points (including root points) is joined by an internal path. Examples are given in Fig. 2D–F.

### 3. *Renormalization of the virial expansion: free energy*

Introduce formally a reference system[3], characterized by the potential energy $\varphi^0(\boldsymbol{r}^N)$ or, simpler, by the pair interaction $V^0(r)$, and write:

$$\begin{aligned} V(r) &= V^0(r)+[V(r)-V^0(r)] \equiv V^0(r)+W(r), \\ f(r) &= f^0(r)+e(r),\ e(r) = e^{-V^0(r)/kT}f^1(r), \\ f^0(r) &= e^{-V^0(r)/kT}-1, f^1(r) = e^{-W(r)/kT}-1. \end{aligned} \tag{3.1}$$

The splitting of the Mayer function $f(r)$ into two parts, $f^0(r)$ of the reference system, and $e(r)$ of the remainder, is equivalent to considering the graphs corresponding to $V_m(\boldsymbol{r}^m)$ as being built of two kinds of lines (bicoloured lines), one kind imparting the factor $f_{ij}^0$, the other $-e_{ij}$. The function $V_m(\boldsymbol{r}^m)$ may thus be written as:

$$\begin{aligned} V_m(\boldsymbol{r}^m) &= \sum_{\{S_m\}} \prod_{S_m} (f_{ij}^0+e_{ij}) = \\ &= V_m^0(\boldsymbol{r}^m)+E_m(\boldsymbol{r}^m), \end{aligned} \tag{3.2}$$

where $V_m^0(\boldsymbol{r}^m)$ leads to the $m$-th virial coefficient of the reference system, $C_m^0$, and

$$E_m(\boldsymbol{r}^m) = \sum_{\{S_m\}} \left[\prod_{S_m} (f_{ij}^0+e_{ij}) - \prod_{S_m} f_{ij}^0\right] \tag{3.3}$$

is given by these from all double-linked graphs $S_m$, which contain at least one line $e_{ij}$. Relation (3.2) leads to the splitting of the free energy:

$$A = A_0+kT\sum_{m=2}^{\infty} C_m^1\left(\frac{1}{v}\right)^{m-1} = A_0+A_1, \tag{3.4}$$

where

$$A_0 = A_{id}+kT\sum_{m=2}^{\infty} C_m^0\left(\frac{1}{v}\right)^{m-1} \tag{3.5}$$

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[3] The quantities referring to the reference system will be denoted by the superscript or subscript 0. Usually, one considers as the reference system the one of hard spheres, but the formalism introduced here is quite general and holds for any (sensible) form of $V^0(r)$, as long as $\varphi^0(\boldsymbol{r}^N)$ is pairwise additive. The properties of the reference system are assumed to be known.

is the free energy of the reference system (this is assumed to be known), whereas $C_m^1$ are given by (2.4) with $E_m(\boldsymbol{r}^m)$ replacing $V_m(\boldsymbol{r}^m)$.

We shall now regroup the virial series of $A_1$, in order to make most of the assumed knowledge of the properties of the reference system. First, define (*i*) the *e*-point (or the basic point) of the graph as the point to which at least one *e*-line is connected (the notion of *e*-lines and $f^0$-lines is self-explaining), and (*ii*) the *e*-structure of a given graph as the topological structure with respect to *e*-points and *e*-lines. These *e*-lines may be connected with each other either directly (two or more *e*-lines with one *e*-point in common), or

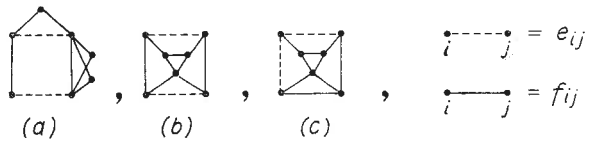


Fig. 3. Graphs a) and b) possess the same *e*-structure, which is different from the *e*-structure of the graph c)

through a path of $f^0$-lines: both these cases form different basic structures. Some simple examples are given in Fig. 3. The collection of all possible graphs with the same *e*-structure sums up to the new *e*-graph, defined by its topology with respect to *e*-points and *e*-lines.

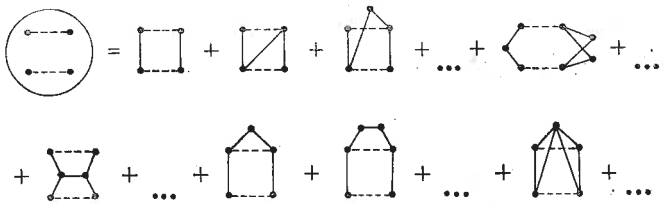

Fig. 4. Construction of the *e*-graph

It is obvious that such regrouping (illustrated in Fig. 4) of the infinite set of original graphs (*i. e.*, these from (3.3)) is unique.

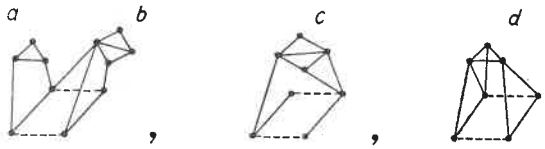


Fig. 5. Examples of side fragments: a) and c) are the pair side fragments, b) and d) — multiple ones

Introduce further auxiliary definitions (examples are presented in Fig. 5):

(*i*) a fragment of a graph (original one), which contains no *e*-point is a side fragment;

(*ii*) a sum of different side-fragments attached (by $f^0$-lines) to a given group of *e*-points is a side structure;

(*iii*) a side structure attached only to a given pair of *e*-points is a pair side structure; otherwise it is a multiple (triple, quadruple, *etc.*) side structure.

A set of $s$ (labeled) $e$-points of a given $e$-graph may be considered as a set of root points for all the side structures, which thus sum up to various $m$-particle ($2 \leqslant m \leqslant s$) distribution or/and correlation functions of the reference system. It is convenient, by the use of the product theorem, to separate out the contributions from all the pair side structures; the pair side structures attached to a given pair of $e$-points sum up to the function $\bar{N}_2^0(r_{ij})$, when the pair $(i, j)$ is connected through the $e$-line, and to a slightly more compli-

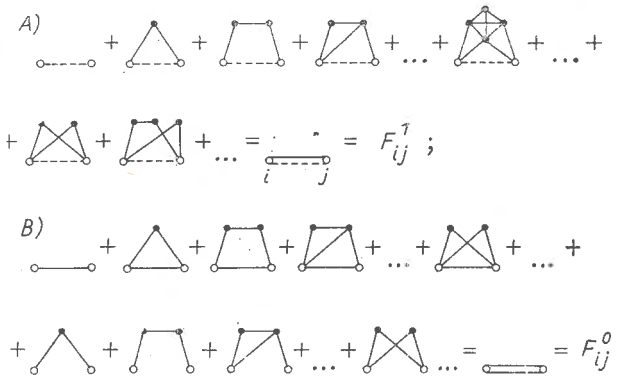


Fig. 6. Summation of the pair side structures

cated form containing $\bar{N}_2^0(r_{ij})$, when otherwise. This is illustrated in Fig. 6 (*cf.* Eq. (2.7) and Fig. 2B).

We define the renormalized virial graphs $\sigma_m$ as $e$-graphs completed by drawing — in all possible ways — the lines representing the attached pair structures. The $e$-line together with the pair side structure parallel to it imparts the factor $F_{ij}^1$ and will be called an $F^1$-line, whereas the line representing the pair side structure attached to two $e$-points not connected by the $e$-line imparts the factor $F_{ij}^0$ ($F^0$-line), with (*cf.* Fig. 6):

$$F^1(r) = e(r)\bar{N}_2^0(r) = f^1(r)g^0(r),$$
$$F^0(r) = f^0(r)\bar{N}_2^0(r) + [\bar{N}_2^0(r) - 1] = g^0(r) - 1. \tag{3.6}$$

The construction of the renormalized virial graphs $\sigma_4$ is shown in Fig. 7. It is seen that the graphs $\sigma_m$ are not necessarily linked ones. However, they proceed from the original

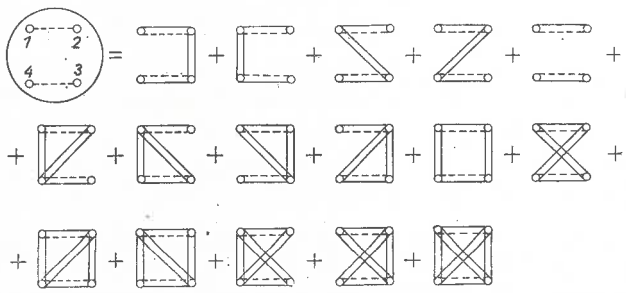


Fig. 7. Renormalized labeled virial graphs corresponding to a given labeled $e$-graph

graphs $S_m$ which must be double linked, and this fact influences the structure of the multiple side structures which are in fact attached to the $\sigma_m$ graphs. We may discern two different cases:

(*i*) the renormalized graph $\sigma_m$ is double linked: thus all possible side fragments sum up to the $m$-particle correlation function $N_m^0(r^m)$;

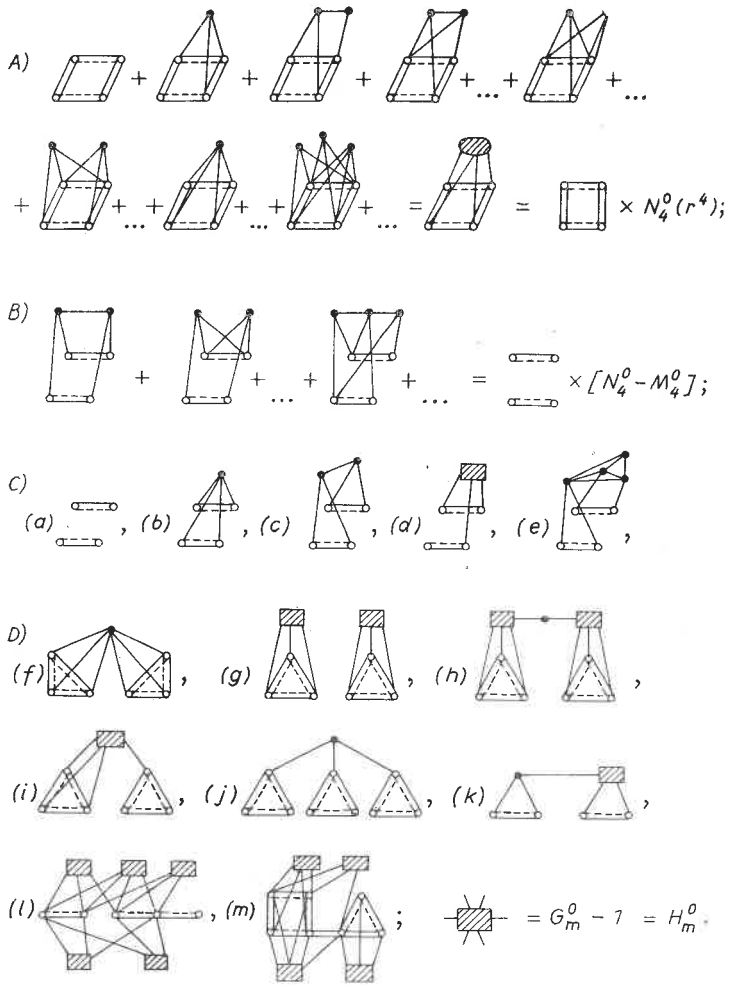


Fig. 8. Summations of multiple side fragments: A) the case when the renormalized $s_4$ graph is double linked; B) the case when the renormalized $s_4$ graph is disjoint; C) examples of graphs $M_4^0$ lacking from $N_4^0$ in the case B); D) examples of more complicated graphs describing different $M_m^0$

(*ii*) the renormalized graph $\sigma_m$ is not double-linked: thus the side fragments must have such a structure that the original graph remains double linked. In other words, in the side structures some side fragments are lacking, compared with the case (*i*). This is illustrated in Fig. 8.

The renormalized virial expansion may thus be written in the form:

$$A = A_0 + kT \sum_{m=2}^{\infty} D_m(T, v) \left(\frac{1}{v}\right)^{m-1}, \tag{3.7}$$

$$D_m = - \lim_{V \to \infty} \frac{1}{V} \frac{1}{m!} \int_V \ldots \int d\boldsymbol{r}_1 \ldots d\boldsymbol{r}_m \{T_m(\boldsymbol{r}^m) N_m^0(\boldsymbol{r}^m) + \Theta_m(\boldsymbol{r}^m)\}, \tag{3.8}$$

where

$$T_m(\boldsymbol{r}^m) = \sum_{\{s_m\}} \prod_{s_m} (F^1, F^0)_{ij} \tag{3.9}$$

$$\Theta_m(\boldsymbol{r}^m) = \sum_{\{u_m\}} [N_m^0(\boldsymbol{r}^m) - M_m^0(u_m; \boldsymbol{r}^m)] \prod_{u_m} (F^1, F^0)_{ij} \tag{3.10}$$

$$\{u_m\} = \{\sigma_m\} - \{s_m\};$$

the sum in (3.9) is the sum over all graphs $\sigma_m$ which are double-linked, whereas the sum in (3.10) is over all remaining graphs from $\{\sigma_m\}$.

The function $M_m^0$, which depends on the detailed structure of a given graph $u_m$, represents the sum of contributions from side fragments which are lacking in $N_m^0$ according to the preceeding analysis, and has a rather complicated form for a general type of a $u_m$ graph. $M_m^0(u_m)$ may be found by drawing all possible graphs composed of side structures attached in all possible ways to a graph $u_m$, such that the graph remains single-linked or disjoint; care must be taken to avoid repetitions of the same fragments in different structures (*cf.* Fig. 9). Some examples of such diagrams are given in Fig. 8C and D; the contributions from them to $M_m^0$ are:

$$\text{(a)} = 1; \quad \text{(b)} = \int d\boldsymbol{r}_5 F_{15}^0 F_{25}^0 F_{35}^0 F_{45}^0;$$

$$\text{(d)} = H_3^0(123); \quad \text{(f)} = \int d\boldsymbol{r}_7 \prod_{i=1}^{6} F_{i7}^0;$$

$$\text{(g)} = H_3^0(123) H_3^0(456); \quad \text{(h)} = \int d\boldsymbol{r}_7 H_4^0(1237) H_4^0(4567);$$

$$\text{(i)} = H_4^0(1234); \quad \text{(j)} = \int d\boldsymbol{r}_{10} F_{1,10}^0 F_{2,10}^0 F_{3,10}^0;$$

$$\text{(k)} = \int d\boldsymbol{r}_5 F_{15}^0 F_{25}^0 H_3^0(345);$$

$$\text{(l)} = H_3^0(123) H_3^0(124) H_3^0(134) H_3^0(234) H_4^0(1234);$$

$$\text{(m)} = H_5^0(12345) H_4^0(1234) H_3^0(125) H_3^0(567); \tag{3.11}$$

where

$$H_m^0(\boldsymbol{r}^m) = G_m^0(\boldsymbol{r}^m) - 1, \quad G_m^0(ij\ldots l) = G_m^0(\boldsymbol{r}_i, \boldsymbol{r}_j, \ldots, \boldsymbol{r}_l);$$

the graphs (c) and (e) are contained in the more general structure (k).

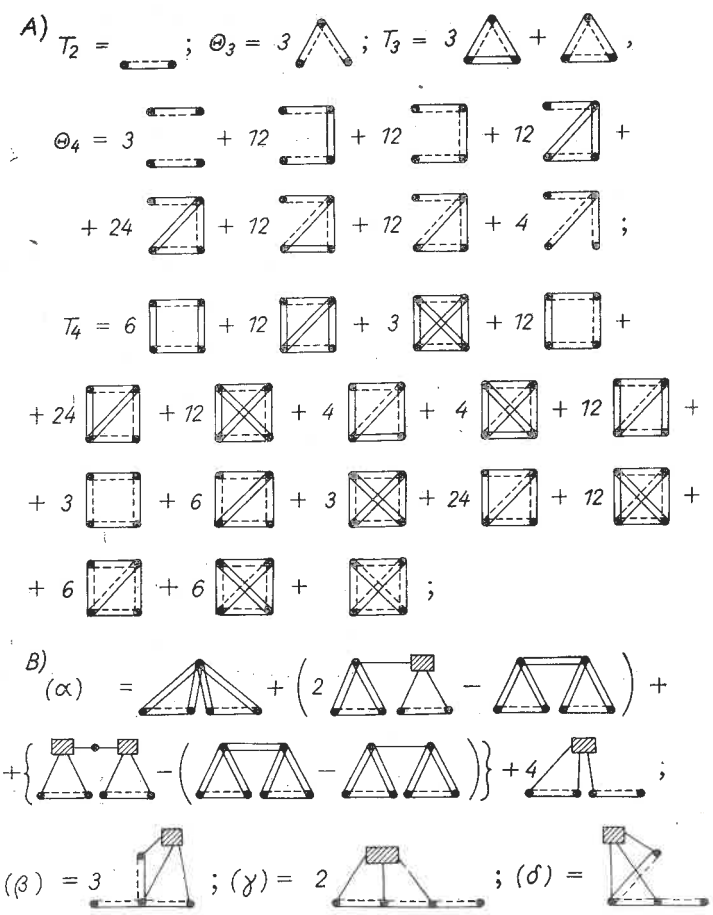

Fig. 9. A) Renormalized unlabeled virial graphs (basic structures) up to 4-th order, together with their combinatorial factors; B) side structures for functions $M_4^0$, for a given labeling of basic structure

To end this Section, we write explicitly the first few coefficients of the renormalized virial expansion of the Helmholtz free energy (the corresponding graphs are given in Fig. 9):

$$D_2 = -\tfrac{1}{2}\int dr F^1(r),$$

$$T_3 = F^1_{12}F^1_{23}(3F^0_{31}+F^1_{31}),$$

$$\Theta_3 = 3F^1_{12}F^1_{23}[N^0_3(123)-1],$$

$$T_4 = F^1_{12}F^1_{23}F^1_{34}F^1_{41}F^1_{13}F^1_{24}+3F^1_{12}F^1_{34}F^0_{23}F^0_{41}(2+4F^0_{13}+F^0_{13}F^0_{24})+$$

$$+12F^1_{12}F^1_{24}F^1_{34}F^0_{41}[F^0_{23}+F^1_{23}(2+F^0_{13})]+3F^1_{12}F^1_{23}F^1_{34}(F^1_{41}+4F^0_{41})\times$$

$$\times(1+2F^0_{13}+F^0_{13}F^0_{24})+2F^1_{12}F^1_{23}F^1_{24}(1+F^0_{13})\,(2F^0_{34}F^0_{41}+3F^1_{34}F^1_{41}),$$

$$\Theta_4 = 3F^1_{12}F^1_{34}\tilde{M}^0_4(\alpha; r^4)+4F^1_{14}F^1_{24}F^1_{34}\tilde{M}^0_4(\beta; r^4)+$$

$$+12F^1_{12}F^1_{34}(F^1_{23}+F^0_{23})\tilde{M}^0_4(\gamma; r^4)+$$

$$+12F^1_{12}[F^1_{34}F^0_{24}(F^0_{23}+2F^1_{23})+F^1_{23}F^1_{24}(F^0_{34}+F^1_{34})]\tilde{M}^0_4(\delta; r^4),$$

where $\tilde{M}^0 = N^0-M^0$,

$$M^0_4(\alpha; r^4) = 1+4H^0_3(123)+\frac{1}{5}\frac{1}{v}\int dr_5\left\{[F^0_{15}F^0_{25}+H^0_3(125)]\,[F^0_{35}F^0_{45}+\right.$$

$$\left.+H^0_3(345)]-\frac{1}{6v}\int dr_6F^0_{15}F^0_{25}(2F^0_{56}-f^0_{56})F^0_{36}F^0_{46}\right\},$$

$$M^0_4(\beta; r^4) = 1+3H^0_3(123), \quad M^0_4(\gamma; r^4) = 1+2H^0_3(123),$$

$$M^0_4(\delta; r^4) = 1+H^0_3(123). \tag{3.12}$$

### 4. *Renormalization of the virial expansion: distribution functions*

The renormalized virial expansion for $s$-particle distribution and correlation functions may be found by the use of techniques similar to that used in the preceding Section. Splitting the potential and the Mayer functions according to (3.1), we get from (2.11)–(2.15):

$$n_s(r^s) = \prod_{\{i,j\}\subset\{s\}} e^{-W(r_{ij})/kT}\{n^0_s(r^s)+v^{-s}\prod_{\{i,j\}\subset\{s\}} e^{-V^0(r_{ij})/kT}\sum_{k=1}^{\infty}\delta^s_k(r^s)v^{-k}\}, \tag{4.1}$$

$$N_s(r^s) = N^0_s(r^s)+\sum_{k=1}^{\infty}\alpha^s_k(r^s)v^{-k}, \tag{4.2}$$

$$G_s(r^s) = G^0_s(r^s)+\sum_{k=1}^{\infty}\beta^s_k(r^s)v^{-k}, \tag{4.3}$$

$$h_s(r^s) = h^0_s(r^s)+\sum_{k=1}^{\infty}\gamma^s_k(r^s)v^{-k}, \tag{4.4}$$

with

$$\delta^s_k(r^s) = \delta^s_k(T, v; r^s) =$$

$$= \frac{1}{k!}\int dr_{s+1}\ldots\int dr_{s+k}\sum_{\{Q_k{}^s\}}\left[\prod_{Q_k{}^s}(f^0_{ij}+e_{ij})-\prod_{Q_k{}^s}f^0_{ij}\right], \tag{4.5}$$

and with $\alpha^s_k(r^s)$, $\beta^s_k(r^s)$, and $\gamma^s_k(r^s)$ given by analogous formulae, with summations ove appropriate sets of graphs $\{N^s_k\}$, $\{M^s_k\}$, and $\{P^s_k\}$, respectively; every of these graphs must contain at least one line $e_{ij}$.

We now rearrange the above sums in the same way as the free energy graphs. The only difference is caused by the presence of the root points, which implies the following:

(*i*) the root points cannot be included in side fragments;

(*ii*) the side structures attached to root points only give exactly the virial expansions of the appropriate functions of the reference system;

(*iii*) when various graphs (analogous to the double-linked graphs describing $T_m$ and the remaining graphs describing $\Theta_m$ in (3.8)) are built, the set of root points is to be considered as a completely linked fragment;

(*iv*) only internal points of the basic structure must be *e*-points, *i.e.*, the rule that to every point at least one $F^1$-line (*e*-line) must be attached does not apply to root points.

Keeping in mind the above remarks, and separating out the pair side structures, we get:

$$n_s(\boldsymbol{r}^s) = n_s^0(\boldsymbol{r}^s) \prod_{\{i,j\} \subset \{s\}} e^{-W(r_{ij})/kT}\{1 + \sum_{k=1}^{\infty} D_k^s(\boldsymbol{r}^s) v^{-k}\}, \tag{4.6}$$

with

$$D_k^s(\boldsymbol{r}^s) = D_k^s(T, v; \boldsymbol{r}^s) =$$

$$= \frac{1}{k!} \frac{1}{N_s^0(\boldsymbol{r}^s)} \int d\boldsymbol{r}_{s+1} \ldots \int d\boldsymbol{r}_{s+k}\{W_k^s(\boldsymbol{r}^{s+k}) N_{s+k}^0(\boldsymbol{r}^{s+k}) + \Omega_k^s(\boldsymbol{r}^{s+k})\}, \tag{4.7}$$

$$W_k^s(\boldsymbol{r}^{s+k}) = \sum_{\{q_k^s\}} \prod_{q_k^s} (F^1, F^0)_{ij}, \tag{4.8}$$

$$\Omega_k^s(\boldsymbol{r}^{k+s}) = \sum_{\{\omega_k^s\}} [N_{s+k}^0(\boldsymbol{r}^{s+k}) - I_{s+k}^0(\omega_k^s; \boldsymbol{r}^{s+k})] \prod_{\omega_k^s} (F^1, F^0)_{ij}, \tag{4.9}$$

where the graphs $\{q_k^s\}$ are the graphs $\{Q_k^s\}$ (*cf.* Section 2) with bicoloured lines ($F^1$- and $F^0$-lines), fulfilling the rule (*iv*) above, $\{\omega_k^s\} = \{g_k^s\} - \{q_k^s\}$, and the graphs $\{g_k^s\}$ are defined as composed of $s$ root points, $k$ internal points, with bicoloured lines, fulfilling the rule (*iv*), and (after insertions of the lines between root points) not necessarily double-linked. The function $I_{s+k}^0(\omega_k^s)$, defined in analogy to the function $M_m^0(u_m)$ in (3.10), depends on the detailed structure of the graph $\omega_k^s$, and represents the sum of contributions from all side structures which cannot be contained in $N_{k+s}^0$, because the graph $\omega_k^s$ with such side structures does not exist in the original virial expansion (2.11) of $n_s(\boldsymbol{r}^s)$ (*i.e.*, such a graph does not belong to $\{Q_k^s\}$). Finally, the factor $1/N_s^0(\boldsymbol{r}^s)$ in (4.7) should in fact be understood as the lack of appropriate factors corresponding to $N_s^0(\boldsymbol{r}^s)$ in the foregoing functions $N_{s+k}^0$ and $I_{s+k}^0$, *i.e.*,

$$N_{s+k}^0(\boldsymbol{r}^{s+k})/N_s^0(\boldsymbol{r}^s) = \prod_{\{l\} \subset \{s+k\}} G_l^0(\boldsymbol{r}^l), \quad l > 3, \quad \{l\} \neq \{s\}, \tag{4.10}$$

and similarly for $I_{s+k}^0/N_s^0$.

Because of the presence of the factors $N_{s+k}^0$, and $(N_{s+k}^0 - I_{s+k}^0)$, multiplying the contributions from various graphs in formulae (4.7), (4.9), the product theorem does not hold for these graphs, and analogous expansions for the correlation and pseudopotential functions cannot be obtained directly from the renormalized virial expansion of $n_s$, Eqs

(4.6)–(4.9). These expansions must thus be found by direct rearrangements of the graph representations of (4.2)–(4.4). Taking into account the definitions (2.8)–(2.10), and the definitions of the classes of graphs $\{N_k^s\}$, $\{M_k^s\}$, $\{P_k^s\}$, we get:

$$N_s(\boldsymbol{r}^s) = N_s^0(\boldsymbol{r}^s) + \sum_{k=1}^{\infty} A_k^s(\boldsymbol{r}^{s+k}) v^{-k}, \tag{4.11}$$

$$G_s(\boldsymbol{r}^s) = G_s^0(\boldsymbol{r}^s)\,[1 + \sum_{k=1}^{\infty} B_k^s(\boldsymbol{r}^{s+k}) v^{-k}], \tag{4.12}$$

$$h_s(\boldsymbol{r}^s) = h_s^0(\boldsymbol{r}^s) + \sum_{k=1}^{\infty} C_k^s(\boldsymbol{r}^{s+k}) v^{-k}, \tag{4.13}$$

with

$$A_k^s(\boldsymbol{r}^{s+k}) = A_k^s(T, v; \boldsymbol{r}^{s+k}) =$$

$$= \frac{1}{k!} \int d\boldsymbol{r}_{s+1} \ldots \int d\boldsymbol{r}_{s+k} [X_k^s(\boldsymbol{r}^{s+k}) N_{s+k}^0(\boldsymbol{r}^{s+k}) + \Xi_k^s(\boldsymbol{r}^{s+k})], \tag{4.14}$$

$$B_k^s(T, v; \boldsymbol{r}^{s+k}) =$$

$$= \frac{1}{k!} \frac{1}{N_s^0(\boldsymbol{r}^s)} \int d\boldsymbol{r}_{s+1} \ldots \int d\boldsymbol{r}_{s+k} [Y_k^s(\boldsymbol{r}^{s+k}) N_{s+k}^0(\boldsymbol{r}^{s+k}) + \Phi_k^s(\boldsymbol{r}^{s+k})\}, \tag{4.15}$$

$$C_k^s(T, v; \boldsymbol{r}^{s+k}) =$$

$$= \frac{1}{k!} \frac{1}{N_s^0(\boldsymbol{r}^s)} \int d\boldsymbol{r}_{s+1} \ldots \int d\boldsymbol{r}_{s+k} \{Z_k^s(\boldsymbol{r}^{s+k}) N_{s+k}^0(\boldsymbol{r}^{s+k}) + \Psi_k^s(\boldsymbol{r}^{s+k})\}, \tag{4.16}$$

$$\Xi_k^s(\boldsymbol{r}^{s+k}) = \sum_{\{v_k^s\}} [N_{s+k}^0(\boldsymbol{r}^{s+k}) - J_{s+k}^0(v_k^s; \boldsymbol{r}^{s+k})] \prod_{v_k^s} (F^1, F^0)_{ij},$$

$$X_k^s(\boldsymbol{r}^{s+k}) = \sum_{\{n_k^s\}} \prod_{n_k^s} (F^1, F^0)_{ij}, \tag{4.17}$$

$$\Phi_k^s(\ ^{s+k}) = \sum_{\{\mu_k^s\}} [N_{s+k}^0(\boldsymbol{r}^{s+k}) - K_{s+k}^0(\mu_k^s; \boldsymbol{r}^{s+k})] \prod_{\mu_k^s} (F^1, F^0)_{ij},$$

$$Y_k^s(\boldsymbol{r}^{s+k}) = \sum_{\{m_k^s\}} \prod_{m_k^s} (F^1, F^0)_{ij}, \tag{4.18}$$

$$\Psi_k^s(\boldsymbol{r}^{s+k}) = \sum_{\{\pi_k^s\}} [N_{s+k}^0(\boldsymbol{r}^{s+k}) - L_{s+k}^0(\pi_k^s; \boldsymbol{r}^{s+k})] \prod_{\pi_k^s} (F^1, F^0)_{ij},$$

$$Z_k^s(\boldsymbol{r}^{s+k}) = \sum_{\{p_k^s\}} \prod_{p_k^s} (F^1, F^0)_{ij}. \tag{4.19}$$

Here $\{v_k^s\} = \{g_k^s\} - \{n_k^s\}$, $\{\mu_k^s\} = \{g_k^s\} - \{m_k^s\}$, $\{\pi_k^s\} = \{g_k^s\} - \{p_k^s\}$, and the graphs $\{n_k^s\}$, $\{m_k^s\}$, $\{p_k^s\}$ are defined as the graphs $\{N_k^s\}$, $\{M_k^s\}$, $\{P_k^s\}$, respectively, with bicoloured lines, and fulfilling the rule (*iv*) above. The functions $J^0$, $K^0$, $L^0$ are analogous to the function $I^0$ from (4.9),

and are given by all the side structures which must be removed from $N^0_{s+k}$, according to the definition of an appropriate class of original graphs. Note that the graphs and the side structures which are allowed, for example, in the virial expansion of $N_s$, are excluded from the virial expansion of $h_s$, and thus the class $\{\pi^s_k\}$ contains some graphs from the class $\{m^s_k\}$, *etc.*

The most important of all these functions is perhaps the radial distribution function $g(r)$, and the pair pseudopotential $h(r)$, and thus we write down, as an example of the application of the general formulae obtained in this Section, the first few renormalized virial coefficients for these functions:

$$h_2(r_{12}) = h_2^0(r_{12}) + h_2^{(1)}(r_{12}) + h_2^{(2)}(r_{12}) + g^{(2)}(r_{12}), \tag{4.20}$$

$$g(r_{12}) = g^0(r_{12}) \exp\left\{-\frac{W(r_{12})}{kT} + h_2(r_{12}) - h_2^0(r_{12})\right\} =$$

$$= g^0(r_{12}) e^{-W(r_{12})/kT}\{1 + h_2^{(1)}(r_{12}) + g^{(1)}(r_{12}) + g^{(2)}(r_{12})\}, \tag{4.21}$$

$$h_2^{(1)}(r_{12}) = \frac{1}{v}\int dr_3 (F^1_{13}F^0_{32} + F^0_{13}F^1_{32} + F^1_{13}F^1_{32}) N^0_3(123) +$$

$$+ \frac{1}{2v^2}\int dr_3 \int dr_4 [(F^0_{13} + F^1_{13})F^1_{34}(F^0_{42} + F^1_{42}) + F^1_{13}F^0_{34}F^1_{42}] (1 + F^0_{32} +$$

$$+ F^1_{32})(1 + F^0_{14} + F^1_{14}) N^0_4(1234) + \ldots \tag{4.22}$$

$$h_2^{(2)}(r_{12}) = \frac{1}{2v^2}\int dr_3 \int dr_4 [2F^1_{13}F^1_{24}(1 + F^1_{32} + F^0_{32} + F^1_{14} + F^0_{14}) +$$

$$+ 2F^0_{13}F^1_{32}F^1_{24} + 2F^1_{13}F^1_{14}F^0_{24} + (F^1_{13}F^0_{32} + F^0_{13}F^1_{32} + F^1_{13}F^1_{32})(F^1_{14}F^0_{42} +$$

$$+ F^0_{14}F^1_{42} + F^1_{14}F^1_{42})] [N^0_4(1234) - 1 - H^0_3(132)H^0_3(142)] + \ldots \tag{4.23}$$

$$g^{(1)}(r_{12}) = \frac{1}{2v^2}\int dr_3 (F^1_{13}F^0_{32} + F^0_{13}F^1_{32} + F^1_{13}F^1_{32}) \int dr_4 (F^1_{14}F^0_{42} +$$

$$+ F^0_{14}F^1_{42} + F^1_{14}F^1_{42}) N^0_4(1234) + \ldots \tag{4.24}$$

$$g^{(2)}(r_{12}) = \frac{1}{v}\int dr_3 (F^1_{13} + F^1_{32}) H^0_3(123) + \frac{1}{2v^2}\int dr_3 \int dr_4 \{F^1_{34}[N^0_4(1234) -$$

$$- 1 - H^0_3(134) - H^0_3(234) - 2H^0_3(123)] + [(F^1_{13} + F^0_{13})F^1_{34}(2 + F^1_{14} +$$

$$+ F^0_{14}) + F^1_{13}F^1_{14}F^0_{34}] [N^0_4(1234) - G^0_3(234)] + 2[F^1_{13}F^1_{24} + (F^1_{13}F^1_{23} +$$

$$+ F^0_{13}F^1_{23} + F^1_{13}F^0_{23})(F^1_{43} + F^1_{24}) + F^1_{14}(F^1_{13}F^1_{23} + F^1_{13}F^0_{23} + F^0_{13}F^1_{23})] \times$$

$$\times [N^0_4(1234) - G^0_3(123)] + [(F^1_{23} + F^0_{23})F^1_{34}(2 + F^1_{24} + F^0_{24}) +$$

$$+ F^1_{23}F^1_{24}F^0_{34}] [N^0_4(1234) - G^0_3(234)]\} + \ldots \tag{4.25}$$

The corresponding side structures from $I^0$ and $L^0$ are drawn in Fig. 10. We do not draw explicitly the corresponding basic graphs, because these graphs are rather numerous, whereas their construction is obvious (compare Fig. 2B with Figs 1 and 9A).

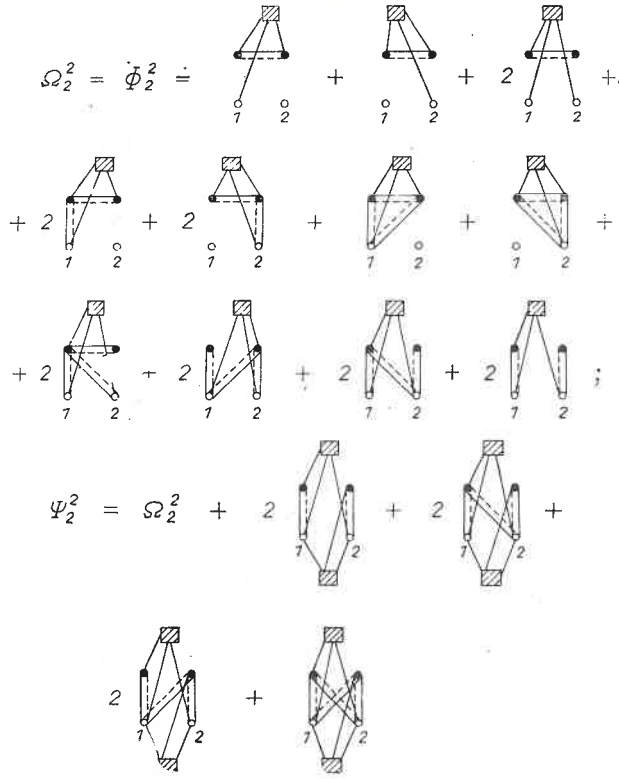

Fig. 10. Side structures which are to be removed from $N_4^0$ in the renormalized virial expansion of the radial distribution function $g(r)$, and the pair pseudopotential $h_2(r)$. Analogous graphs with basic structures containing $F^0$-lines instead of some $F^1$-lines are to be added

The formulae (4.20)–(4.25) illustrate also the differences in the renormalized virial expansion of the functions $G$ and $h$, this difference being not only in the lack of some graphs in the expansion of $h$, but also in the different structures of the functions $I^0$ and $L^0$.

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