

ON THE SUMMATION OF THE URSELL-MAYER CLUSTER
EXPANSION. II. BRANCHED CHAINS

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The infinite subset of graphs, describing the Ursell-Mayer cluster expansion of the equation of state and consisting of mixed Husimi trees built from Cayley trees and simple polygons, is considered. The expressions for the pressure and density of the system of interacting particles as functions of activity are obtained. These expressions are equivalent to the one-chain (OC) approximation of the virial expansion of the equation of state. The results obtained here may be useful for the formal discussion of the phase transitions in the OC approximation on the basis of the Yang-Lee theory.

It is now widely realized that the statistical-mechanical description of phase transitions requires consideration of the infinite range — in one meaning or another — of intermolecular interactions. This may be accomplished either by considering directly the limit of infinite-range (and at the same time infinitely weak) original intermolecular two-body potentials [1-4] or by arriving at the infinite-range effective intermolecular force field by the summations of some infinite subsets of terms describing some formal expansions of the properties of the system under consideration [5-8]. Indeed, we have recently shown [9, 10] that summation of the topologically simplest infinite subset of diagrams (the OC — one-chain — approximation) representing the expansion of the pressure and of radial distribution function [11, 12] leads to approximate formulas which can provide an explicit prediction of the first-order phase transitions with the use of the short-range original intermolecular potential. We have also shown in the preceding paper [13] (hereafter referred to as I) that the still simpler infinite subset of terms — the simple chain (SC) approximation of the cluster Ursell-Mayer expansion [11, 12] also predicts a one phase transition. In this paper we shall perform further summations of some subsets of terms describing the cluster expansion in order to show how the OC approximation is built in this formalism. This procedure will lead to the formulation of the OC approximation in terms of the dependence on activity instead of actual density of the system.

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1. Formalism

We consider — in analogy with I — a system of N identical particles contained in volume Ω , kept at temperature T , and interacting with each other through the short-range pair potential $V(r)$. The thermodynamical limit, $N \rightarrow \infty$, $\Omega \rightarrow \infty$, $\rho = \frac{1}{v} = \frac{N}{\Omega} = \text{finite}$, is assumed. The equation of state (*i.e.*, the relation between the pressure P , temperature T , and density ρ) is expressed in terms of the function $\chi(T, z)$ (which itself is related to the grand-canonical partition function and the Helmholtz free energy; *cf.* I for more details),

$$P = kT\chi(T, z), \quad \rho = \frac{1}{v} = z \left(\frac{\partial \chi}{\partial z} \right)_T, \quad (1.1)$$

where z is the activity (active density, fugacity) of the system. In the Ursell-Mayer cluster expansion the function χ is written in the form:

$$\chi(T, z) = \sum_{l=1}^{\infty} b_l(T) z^l, \quad (1.2)$$

$$b_l(T) = \lim_{\Omega \rightarrow \infty} \frac{1}{\Omega} \frac{1}{l!} \int_{\Omega} \dots \int_{\Omega} d\mathbf{r}_1^* \dots d\mathbf{r}_l^* U_l(\mathbf{r}_1, \dots, \mathbf{r}_l), \quad (1.3)$$

where U_l , the Ursell cluster functions, are expressed in terms of the finite sets of the l -point connected graphs (*cf.* Ref. [12] and I for more details). The expansion (1.2) is thus represented by an infinite set of labeled linear connected graphs.

The SC approximation considered in I consists in neglecting all the graphs of the expansion (1.2) except the simple polygons, *i.e.*, taking into account only one graph for every b_l . On the other hand, the OC approximation [9, 10] is constructed by the summation of topologically identical subset of graphs, which represents, however, the virial expansion, *i.e.*, it represents physically different quantities. Namely, in the virial expansion formalism [12] the pressure P is expressed in the form

$$\frac{P}{kT} = \rho + \sum_{m=2}^{\infty} B_m(T) \rho^m, \quad (1.4)$$

where B_m , the virial coefficients, are expressed in terms of m -point linear biconnected graphs, which topologically belong to the subset of the whole set of linear connected graphs describing the expansion (1.2). The relation between the expressions (1.4) and (1.2) may thus be stated as follows:

(i) every biconnected graph G_s of the virial expansion (1.4) proceeds from the whole infinite family (subset) of connected graphs of the cluster expansion (1.2). The latter graphs are pure Husimi trees (in the language of the theory of graphs [12]) built of 1, 2, ... graphs G_s , and

(ii) every group (subset) of different biconnected graphs G_s, G_t, \dots of the virial expansion (1.4) proceeds from the whole infinite family of mixed Husimi trees connected

graphs of the cluster expansion (1.2) built of all possible combinations of 1, 2, ... graphs G_s, G_r, \dots

A simple illustration will be given below.

According to the above statements, the OC approximation of the virial expansion will be expressed in the cluster expansion (1.2) by the infinite subset $\{H_0\}$ of connected graphs which are mixed Husimi trees built of all the simple polygons (including the simple line, *i.e.*, two-point one-line graph). The task of this paper is to perform the summation of the contributions from the graphs belonging to $\{H_0\}$.

2. Cayley trees

Let us start with the summation of the contributions from the subset $\{C\}$ composed of Cayley trees, *i.e.*, from connected graphs built of simple lines only (*cf.* Fig. 1). This problem is quite simple: the contribution to b_l from a given l -point *i.e.*, containing $l-1$ lines labeled Cayley tree is:

$$\frac{1}{l!} \beta_1^{l-1}, \beta_1 = \int dr f(r), f(r) = e^{-V(r)/kT} - 1. \quad (2.1)$$

On the other hand, an l -point Cayley tree may be labeled in l^{l-2} topologically different ways [12]. The total contribution to (1.2) from all the Cayley trees is thus (including the first term $b_1 z = z$):

$$\chi_{C.T.} = z + \sum_{l=2}^{\infty} \frac{l^{l-2}}{l!} z^l \beta_1^{l-1} = z + \beta_1^{-1} \varphi_{-2}(z\beta_1), \quad (2.2)$$

and, from (1.1),

$$\frac{P}{kT} = z + \beta_1^{-1} \varphi_{-2}(z\beta_1), \quad (2.3)$$

$$\varrho = z + \beta_1^{-1} [\varphi_{-1}(z\beta_1) - z\beta_1], \quad (2.4)$$

which describe in this approximation the pressure and the density as functions of the activity z . Definitions and some properties of the functions $\varphi_{-k}(x)$ are given in the Appendix. For our present purposes the following relation will be useful:

$$\varphi_{-2}(x) = \varphi_{-1}(x) - \frac{1}{2} [\varphi_{-1}(x)]^2 - x. \quad (2.5)$$

Namely, making use of (2.4) and (2.5), we get

$$\varphi_{-2}(z\beta_1) = \beta_1 \varrho - \frac{1}{2} (\beta_1 \varrho)^2 - z\beta_1, \quad (2.6)$$

which, together with (2.3), leads to the equation of state:

$$\frac{P}{kT} = \varrho - \frac{1}{2} \beta_1 \varrho^2, \quad (2.7)$$

being exactly the first two terms of the virial expansion (1.4) with the proper value of the second virial coefficient, $B_2(T) = \frac{1}{2}\beta_1(T)$. This illustrates the first of the statements formulated in the preceding Section.

It is also possible in this case to write down explicitly the formula inverse to (2.4), *i.e.*, the explicit dependence of the active density z on the actual density ϱ . Namely, (*cf.* Appendix), the function $\varphi_{-1}(x)$ fulfills the functional equation:

$$\varphi_{-1}(x) = x \exp \{ \varphi_{-1}(x) \}, \quad (2.8)$$

which, together with (2.4), gives

$$z = \varrho e^{-\beta_1 \varrho}. \quad (2.9)$$

It is easily seen that in this approximation z reaches the maximum value $z_{\max} = 1/e\beta_1$ at $\varrho = 1/\beta_1$, and for higher values of density it decreases.

3. Second-order mixed graphs

The process of building the general subset $\{H_0\}$ of mixed Husimi trees, corresponding to the OC approximation, may be started in several different ways. In this Section we shall describe the construction of a few simpler subsets of mixed graphs, which will be useful later on when constructing a general mixed Husimi tree. Moreover, these contributions may present some interest in themselves, illustrating the process of the passage from the SC to the OC approximations.

We have considered in I the subset $\{R_0\}$ of simple polygons (rings), what leads to the following expressions for the pressure and density of the system:

$$\frac{P(T, z)}{kT} = z - \frac{1}{2} \beta_1 z^2 + R_0(T, z), \quad (3.1)$$

$$\varrho(T, z) = z - \beta_1 z^2 + z R_1(T, z), \quad (3.2)$$

with

$$R_0(T, z) = - \frac{1}{2(2\pi)^3} \int d\mathbf{q} \left\{ \ln |1 - z\gamma(q)| + z\gamma(q) + \frac{1}{2} [z\gamma(q)]^2 \right\}, \quad (3.3)$$

$$R_1(T, z) = \frac{\partial}{\partial z} R_0(T, z), \quad (3.4)$$

$$\gamma(q) = \int d\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} f(r). \quad (3.5)$$

The first two terms of the r.h.s. of (3.1) and (3.2) follow from the first two terms of the expansion (1.2), *i.e.*, from the one-point graph, and from the simple line, these graphs being understood here also to be polygons.

We shall now consider the simplest generalization of the subset $\{R_0\}$: the subset $\{R_l\}$ of polygons to each point of which an arbitrary number (from zero to infinity) of simple lines are attached. From the formal point of view, this is a step towards "dressing" every

point of the polygon into a full Cayley tree; however, the subset $\{R_j\}$ may also be simply interpreted from the physical point of view: it corresponds to the situation when every particle forming the ring feels the presence of all the other particles of the system in such a way as if these remaining particles were not interacting between themselves. Examples of graphs belonging to $\{R_j\}$, as well as to $\{C\}$ and $\{R_0\}$, are presented in Fig. 1.

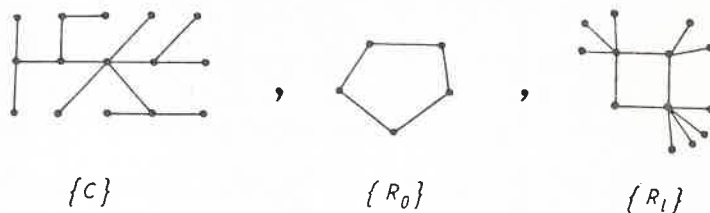


Fig. 1. Examples of graphs belonging to $\{C\}$, $\{R_0\}$, and $\{R_l\}$

Because the contributions from single-connected parts of a graph (*i.e.*, those which may be separated by a single cut at a given point) factorize, the contribution r_l from a given dressed polygon may be written as:

$$r_l = r_0 \beta_1^k,$$

where r_0 is the contribution from the original ("bare") polygon, and β_1 , the contribution from a simple line, is given by (2.1). It remains thus for us to sum up the contributions from all such labeled graphs. This may be done as follows: Every point of the graph from $\{R_0\}$ is associated in the expansion (1.2) with the factor z . Now, instead of considering a given graph from $\{R_0\}$, we consider the whole subset of graphs belonging to $\{R_l\}$ which differ

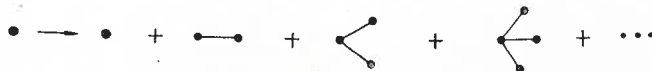


Fig. 2. Renormalization of the point of a ring

between themselves only in the number of simple lines attached to a given point of the ring. This procedure, illustrated in Fig. 2, leads to a renormalization of the factor z associated with the point of the ring¹:

$$z \rightarrow z \sum_{n=0}^{\infty} \frac{1}{n!} (z\beta_1)^n = z e^{z\beta_1}. \quad (3.6)$$

¹ First, we divide all the labeled points into groups: the basic group of m points forming the basic ring, and $m(i = 1, 2, \dots, m)$ groups, each containing l_i points attached to the i -th point of the ring. This may be done in $l!/(m!l_1! \dots l_m!)$ ways; $l = m + l_1 + \dots + l_m$ is the total number of points of the graph. This, together with the factor $1/l!$ in the definition (1.3) of b_1 , leads to (3.6), because an exchange of labels within the group of points attached to the same point of the ring does not lead to a topologically new structure and is thus irrelevant.

We obtain thus, instead of (3.1) and (3.2) (from now on we shall not explicitly indicate the dependence of the functions on temperature):

$$\frac{P}{kT} = ze^{z\beta_1} - \frac{1}{2} \beta_1 z^2 e^{2z\beta_1} + R_0(ze^{z\beta_1}), \quad (3.7)$$

$$\varrho = z(1+z\beta_1)e^{z\beta_1}[1-z\beta_1e^{z\beta_1}+R_1(ze^{z\beta_1})], \quad (3.8)$$

which determine the equation of state in the R_l approximation.

The next possible step is the renormalization (analogous to the above) of the point of the ring by attaching a complete Cayley tree to it. Now, (i) the contribution from a given p -point Cayley tree (including all possible labelings of the points) is $p^{p-2}\beta_1^{p-1}$, (ii) every tree is attached to the given ring-point by the line which brings up the factor β_1 , and which may be attached to any of the tree-points (*i.e.* the tree may be attached to the ring-point in p different ways), and (iii) to every ring-point any number of Cayley trees may be attached. This leads to the renormalization:

$$z \rightarrow z \sum_{l=0}^{\infty} \frac{1}{l!} \left\{ \sum_{p=1}^{\infty} \frac{z^p}{p!} p \beta_1 \cdot p^{p-2} \beta_1^{p-1} \right\}^l = z \exp \{ \varphi_{-1}(z\beta_1) \} \equiv z_t. \quad (3.9)$$

This renormalization may be applied to the terms proceeding from polygons composed of at least three points. The first two terms of the expansion (1.2) may be consistently renormalized here into one Cayley tree, *i.e.* they will be now given by (2.3) and (2.4). The equation of state is thus determined in their approximation by

$$\frac{P}{kT} = z + \beta_1^{-1} \varphi_{-2}(z\beta_1) + R_0(z_t), \quad (3.10)$$

$$\varrho = \beta_1^{-1} \varphi_{-1}(z\beta_1) + R_1(z_t) [(1 + \beta_1 \varphi_0(z\beta_1)) z \exp \{ \varphi_{-1}(z\beta_1) \}]. \quad (3.11)$$

We shall now consider two more subsets which will be useful in the construction of the general subset $\{H_0\}$, namely, the subset $\{CR\}$ composed of Cayley trees dressed into polygons, and $\{RR\}$ composed of polygons dressed into polygons. Examples of graphs belonging to these subsets are given in Fig. 3. The method of calculation is in both cases

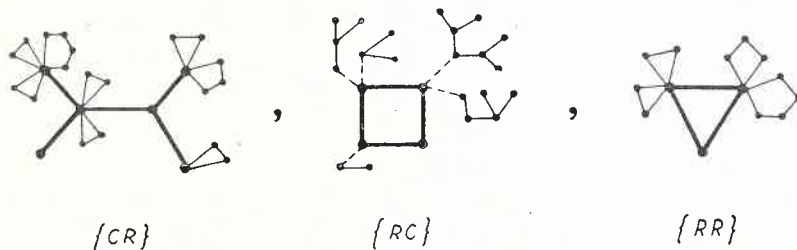


Fig. 3. Examples of graphs belonging to $\{RC\}$, $\{CR\}$, and $\{RR\}$. Heavy lines denote the basic structure of the graph; the dashed lines in RC denote the additional lines joining Cayley trees with the ring-points

similar to that used above, with the one exception that the points of the attachment are now common points of a few structures: the basic one (tree or ring), and the attached polygons². The renormalization is identical for both cases,

$$z \rightarrow z \sum_{n=0}^{\infty} \frac{1}{n!} \left\{ \sum_{m=2}^{\infty} \frac{z^m}{m!} \frac{m!}{2} \frac{1}{(2\pi)^3} \int d\mathbf{q} [\gamma(q)]^{m+1} \right\}^n = z \exp \{R_1(z)\} \equiv z_r. \quad (3.12)$$

For the $\{CR\}$ subset, this renormalization is to be applied to Eq.(2.3) so that the equation of state is given by

$$\frac{P}{kT} = z + \beta_1^{-1} \varphi_{-2}(z_r \beta_1), \quad (3.13)$$

$$\varrho = z + [\beta_1^{-1} \varphi_{-1}(z \beta_1) - z_r] [1 + R_2(z)] \exp \{R_1(z)\}, \quad (3.14)$$

where

$$R_2(T, z) = z \frac{\partial}{\partial z} R_1(T, z). \quad (3.15)$$

For the $\{RR\}$ subset we get from (3.12) and (3.1)

$$\frac{P}{kT} = z_r - \frac{1}{2} \beta_1 z_r^2 + R_0(z_r), \quad (3.16)$$

$$\varrho = [1 - \beta_1 z_r + R_1(z_r)] z_r [1 + R_2(z)]. \quad (3.17)$$

4. Mixed Husimi trees and the OC approximation

The construction of the subset $\{H_0\}$ of mixed Husimi trees, composed of Cayley trees and of polygons (which describe the OC approximation in the cluster expansion formalism) may be accomplished in two ways: either starting from the subset $\{R_0\}$ of pure polygons (rings), or starting from the subset $\{C\}$ of pure Cayley trees. The main procedure will be the renormalization of the points of the graphs in a manner similar to that described in the preceding Section; this renormalization will be done in the iterative way.

Let us start from the subset $\{R_0\}$. First, we renormalize the points of the original (zeroth order) polygons³ dressing them into both Cayley trees and into polygons; these attached structures will be called first-order subgraphs (compare with Eqs (3.12) and (3.9)). This renormalization gives

$$z \rightarrow z \exp \{R_1(z) + \varphi_{-1}(z \beta_1)\} \equiv z_1 = z_r z_e / z. \quad (4.1)$$

² The combinatorial factor of the attached polygon in $m!/2$, instead of $m!/2m$ as for a free polygon, because of the lack of the m -fold symmetry axis.

³ We consider here only the true polygons, containing $m \geq 3$ points; the first two terms of the expansion (1.2) must be considered separately.

Now, we renormalize the points of the structures attached to the original ring by dressing the point of the first-order polygons into second-order Cayley trees and polygons, and dressing the points of the first-order Cayley trees into second-order polygons (a Cayley tree cannot be dressed into another Cayley tree, because it would result in yet another Cayley tree which has been taken into account in the first-order dressing). The result is thus

$$\begin{aligned} z_1 \rightarrow z_2 &\equiv z \exp \{R_1(z_1) + \varphi_{-1}(z_1\beta_1)\} \\ &= z \exp \{R_1(z \exp \{R_1(z) + \varphi_{-1}(z\beta_1)\}) + \varphi_{-1}(z\beta_1 \exp \{R_1(z)\})\}. \end{aligned} \quad (4.2)$$

This procedure is obviously recursive and may be repeated up to infinity, what leads to the final renormalization

$$z \rightarrow x, \quad (4.3)$$

with x given by the solution of the functional-integral equation

$$x = z \exp \{R_1(x) + \varphi_{-1}(x_1)\}, \quad x_1 = z\beta_1 \exp \{R_1(x)\}. \quad (4.4)$$

The graphs constructed in the way described above do not contain simple Cayley trees; also, the first term of the cluster expansion (1.2) has not been taken into account. The contributions from these terms must thus be added to the final expression (*cf.* Eq. (2.3)), so we get

$$\frac{P}{kT} = z + R_0(x) + \beta_1^{-1} \varphi_{-2}(z\beta_1), \quad (4.5)$$

$$\varrho = \beta_1^{-1} \varphi_{-1}(z\beta_1) + R_1(x) z \frac{dx}{dz}, \quad (4.6)$$

and from (4.4),

$$z \frac{dx}{dz} = x \frac{1 + \varphi_0(x_1)}{1 - R_2(x) [1 + \varphi_0(x_1)]}. \quad (4.7)$$

The same procedure may be applied when we take as the starting point the subset $\{C\}$ of pure Cayley trees. In this case, the result is

$$\frac{P}{kT} = z + R_0(x_r) + \beta_1^{-1} \varphi_{-2}(x_1), \quad (4.8)$$

$$\varrho = z + \frac{x_r T_1(x_r)}{1 - R_2(x_r)} + \beta_1^{-1} [\varphi_{-1}(x_1) - x_1] \left[1 + \frac{z}{x} R_2(x) \frac{dx}{dz} \right], \quad (4.9)$$

where x and x_1 are given by (4.4), and x_r is the solution of the equation

$$x_r = z \exp \{R_1(x_r)\}, \quad (4.10)$$

(the second term of the r. h. s. of (4.8) proceeds from the Husimi tree built of m -gons with $m \geq 3$ only). Both these results, Eqs (4.5), (4.6) and (4.8), (4.9), are equivalent, although not identical, because both represent the sum of contributions of the same (infinite) subset $\{H_0\}$ of graphs of the cluster expansion.

5. Final remarks

The equations derived in the preceding Section describe the OC approximation of the equation of state in terms of the cluster expansion, *i. e.* through the dependence on the activity z . Thus, in order to get the equation of state in the form of a single relation between P , ρ , and T , z has to be eliminated from Eq. (4.5) by means of Eq. (4.6), or from Eq. (4.8) by means of Eq. (4.9). The explicit relation expressing z as a function of ρ in the OC approximation may, however, be obtained also in a simpler way, namely, by performing the OC summation for the general expression [12]

$$\ln z = \ln \rho - \sum_{n=1}^{\infty} \beta_n \rho^n, \beta_n(T) = - \frac{n+1}{n} B_{n+1}(T). \quad (5.1)$$

From the OC approximation for B_m [18],

$$B_m = - \frac{m-1}{m} \frac{1}{2(2\pi)^3} \int d\mathbf{q} [\gamma(\mathbf{q})]^m, m \geq 3, B_2 = - \frac{1}{2} \beta_1, \quad (5.2)$$

(β_1 is given by (2.1)), we get

$$z = \rho \exp \{-\beta_1 \rho + R_1(T, z)\}. \quad (5.3)$$

We have shown in I that the SC approximation (the contribution to the cluster expansion from the subset $\{R_0\}$) predicts the existence of one phase transition, whereas the OC approximation of the virial series predicts two phase transitions, and that SC and OC approximations lead to different shapes of the isotherms $P = P(\rho)$. The results obtained in this paper might be used for investigating how the SC isotherms are transformed into OC isotherms when different subsets of graphs are additionally taken into account. This would require, however, rather extensive numerical calculations. Nevertheless, some conclusions may be drawn directly from the expressions obtained here. The series summed into the SC approximation is convergent for the values of z determined by the condition (*cf.* I)

$$|z| < z_{\max} = 1/\text{Max}\{|\gamma(\mathbf{q})|\}. \quad (5.4)$$

For $|z| > z_{\max}$, the expressions for P and ρ (Eqs (3.1)–(3.5)) may be treated as analytic continuations of this series, whereas at the point $z = z_{\max}$ these expressions are singular. Now, we have shown in this paper that retaining more complicated graphs (the dressing of the $\{R_0\}$ graphs) leads to renormalization of the parameter z in the expressions for the pressure, and this changes the expression for the density. This will change the condition (5.4) and the value of z at which the singularity appears. Let us look, for example, at the expression (3.7), representing the subset $\{R_1\}$. The location of the singularity is now determined by

$$\text{Max}\{|\gamma(\mathbf{q})|\} z e^{z\beta_1} = 1, \quad (5.5)$$

hence, it now depends on temperature not only through the temperature dependence of $\gamma(\mathbf{q})$, but also through the temperature dependence of β_1 . The behaviour is even more

complicated when the subsets $\{RC\}$ or $\{RR\}$ are considered; in these cases, the location of the singularity is determined by the conditions:

$$\text{Max}\{|\gamma(q)|\} z \exp\{\varphi_{-1}(z\beta_1)\} = 1, \text{ or } \text{Max}\{|\gamma(q)|\} z \exp\{R_2(z)\} = 1, \quad (5.6)$$

respectively. These conditions may be fulfilled for more than one value of z , depending on the shape of the functions in the exponent. Besides, a new singularity of the pressure will appear here at the point where these functions themselves are singular. In the $\{RR\}$ case, for example, we may expect the existence of two singular points: one when $z \text{Max}\{|\gamma(q)|\} = 1$ (the discontinuity in $R_1(z)$), and the second being at the solution of (5.6).

A more detailed discussion of the formal properties of the singular points of the pressure (or of the function $\chi(T, z)$, *i. e.*, the logarithm of the grand-canonical partition function), considered as an analytic function of the complex variable z , and of their connections with phase transitions in the system, might be performed in terms of the Yang-Lee formalism [14]. The formulas obtained in this work may serve as the starting point for such a discussion. The extension of such a work by retaining even more complicated subsets of graphs also seems possible. This might be done by a determination (and summation) of the cluster graphs corresponding to the hypernetted chain or Percus Yevick approximations [5-8]. Another possible way would be the determination of the OC cluster formulas for the radial distribution function and from it the two-particle effective field potential. The latter would be used iteratively (being dependent on temperature and activity) in the definition of the Mayer function $f(r)$, and thus in the determination of subsequent functions appearing in the formulas of this paper.

APPENDIX

We shall present some properties and relations between the functions connected with Cayley trees used in this paper.

We define the family of functions $\varphi_{-n}(z)$ by their series expansions:

$$\varphi_0 = \sum_{k=1}^{\infty} \frac{k^k}{k!} z^k, \quad \varphi_{-n}(z) = \sum_{k=n}^{\infty} \frac{k^{k-n}}{k!} z^k, \quad n = 1, 2, \dots \quad (A.1)$$

The function $\varphi_{-2}(z)$ is the generating function for the labeled Cayley tree. It is easily proved that these functions fulfill the relations:

$$z \frac{d}{dz} \varphi_{-1}(z) = \varphi_0(z),$$

$$z \frac{d}{dz} \varphi_{-n}(z) = \varphi_{-(n-1)}(z) - \frac{z^{n-1}}{(n-1)!}, \quad n \geq 2. \quad (A.2)$$

The asymptotic behaviour for small z is

$$\varphi(0) = \varphi_{-n}(0) = 0, \quad \lim_{z \rightarrow 0} \frac{1}{z} \varphi_0(z) = 1,$$

$$\lim_{z \rightarrow 0} z^{-n} \varphi_{-n}(z) = \frac{1}{n!}, \quad n \geq 1. \quad (A.3)$$

Let us now determine the radius of convergence of the series (A.1). For sufficiently great values of k , the Stirling approximation may be used for the estimation of the terms (cf. e. g. [15]):

$$k \ln k - k + 1 < \ln k! < k \ln k - k + 1 + 0.5 \ln k,$$

i. e.,

$$k^k e^{-k+1} < k! < k^k \sqrt{k} e^{-k+1} \quad (\text{A.4})$$

and thus

$$\frac{(ze)^k}{ek^n \sqrt{k}} < \frac{k^{k-n}}{k!} z^k < \frac{(ze)^k}{ek^n}, \quad (\text{A.5})$$

which shows that the radius of convergence of the series (A.1) of the variable z is the same as of the geometric series of the variable (ez) ; in other words, the series converge for

$$|z| < 1/e. \quad (\text{A.6})$$

The functions φ_{-n} , φ_0 may also be determined in the following way: from (A.1), $\varphi_{-1}(z)$ may be written in the form:

$$\varphi_{-1}(z) = \sum_{k=1}^{\infty} \frac{z^k}{k!} \left[\frac{d^{k-1}}{dt^{k-1}} e^{kt} \right]_{t=0}, \quad (\text{A.7})$$

which, according to the well-known Lagrange theorem, is the formal solution of the functional equation

$$\varphi_{-1}(z) = z e^{\varphi_{-1}(z)}. \quad (\text{A.8})$$

For real z , this equation has the solutions for $z \leq 1/e$ only, in accordance with (A.6), and $\varphi_{-1}(1/e) = 1$.

Differentiating (A.8), we get the differential equation for $\varphi_{-1}(z)$

$$z(1-\varphi_{-1}) \varphi'_{-1} = \varphi_{-1}. \quad (\text{A.9})$$

Making use of (A.2), we may find the relations between different φ -functions:

$$\varphi_0 = \frac{\varphi_{-1}}{1-\varphi_{-1}}, \quad (\text{A.10})$$

$$\varphi_{-2} = \varphi_{-1} - \frac{1}{2} \varphi_{-1}^2 - z, \quad (\text{A.11})$$

$$\varphi_{-3} = \varphi_{-1} - \frac{3}{4} \varphi_{-1}^2 + \frac{1}{6} \varphi_{-1}^3 - z - \frac{1}{4} z^2, \quad (\text{A.12})$$

etc. (the relations (A.11), (A.12) are obtained by the integration of (A.2) with the use of (A.9) and (A.3)). The relation (A.11) has been used in the Section 2 of this paper.

REFERENCES

- [1] G. E. Uhlenbeck, P. C. Hemmer, in: *Statistical Mechanics of Equilibrium and Non-Equilibrium* (edited by J. Meixner), North-Holland Publ. Co., Amsterdam 1965, p. 241.
- [2] M. Kac, G. E. Uhlenbeck, P. C. Hemmer, *J. Math. Phys.*, **4**, 216, 229 (1963); **5**, 60 (1964).
- [3] G. G. Emch, *J. Math. Phys.*, **8**, 13, 19 (1967).
- [4] N. G. Van Kampen, *Physica*, **48**, 313 (1970).
- [5] J. M. J. VanLeeuwen, J. Groeneveld, J. DeBoer, *Physica*, **25**, 792 (1959).
- [6] T. Morita, *Progr. Theor. Phys.*, **41**, 339 (1969).
- [7] J. K. Percus, G. J. Yevick, *Phys. Rev.*, **110**, 1 (1958).
- [8] G. Stell, *Physica*, **19**, 517 (1963).
- [9] A. Fuliński, *Acta Phys. Polon.*, **A37**, 177, 185 (1970); *Phys. Letters*, **31A**, 176 (1970).
- [10] A. Fuliński, M. Jurkiewicz, *Phys. Letters*, **32A**, 126 (1970); *Acta Phys. Polon.*, (**A39**, 167 1971).
- [11] J. O. Hirschfelder, Ch. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, Inc., New York 1954.
- [12] G. E. Uhlenbeck, G. W. Ford, in: *Studies in Statistical Mechanics* (edited by J. DeBoer and G. E. Uhlenbeck), Vol. I, North-Holland Publ. Co., Amsterdam 1962, Part B.
- [13] A. Fuliński, *Acta Phys. Polon.* **A40**, 221 (1971).
- [14] C. N. Yang, T. D. Lee, *Phys. Rev.*, **87**, 404 (1952); T. D. Lee, C. N. Yang, *ibid.*, 410.
- [15] H. J. G. Hayman, *Statistical Thermodynamics*, Elsevier Publ. Co., Amsterdam—London—New York 1967, p. 229.