Van Kampen, N. G.
1961

Physica 27
783–792

A SIMPLIFIED CLUSTER EXPANSION FOR THE CLASSICAL REAL GAS

by N. G. VAN KAMPEN

Instituut voor Theoretische Fysica der Rijksuniversiteit te Utrecht, Nederland

Synopsis

Mayer's expansion of the partition function of a classical real gas in terms of irreducible cluster integrals is derived by a simpler and more direct method. The two principal features of this method are the following.

(i) The partition function is expanded in an infinite *product* rather than a series. As a result the exponential form is obtained immediately: there is no need to sum up infinite sets of graphs. Disconnected graphs never enter.

(ii) The calculation leads directly to the *canonical* N-particle partition function. Neither the fugacity nor the reducible cluster integrals are introduced.

The same method is also used to find the expansion of the pair-correlation function. Finally it is applied to the partition function of a real gas in an external potential field.

1. *The first approximation* (*second virial coefficient*). In classical theory the problem of finding the equation of state of a real monatomic gas amounts to evaluating the configurational partition function

$$Q_N = \int e^{-\beta(v_{12}+v_{13}+\dots v_{N-1,N})}\, \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2 \dots \mathrm{d}\boldsymbol{r}_N.$$

The domain of this $3N$-dimensional integral is determined by the fact that each particle may move throughout the volume V, irrespective of the positions of the others. Hence the integral may also be regarded as an average over N-particle configurations,

$$Q_N = V^N\, \overline{\varphi_{12}\varphi_{13} \cdots \varphi_{N-1,N}}, \tag{1}$$

where $\varphi_{12} = e^{-\beta v_{12}}$ etc., and the bar denotes the average over all positions of the particles inside V.

The φ's are functions of the random variables $\boldsymbol{r}_1, \dots, \boldsymbol{r}_N$ and $\varphi_{12} \to 1$ as $|\boldsymbol{r}_1 - \boldsymbol{r}_2| \to \infty$. It is clear that φ_{12} and φ_{34} are statistically independent, and also φ_{12} and φ_{13}. Thus

$$\overline{\varphi_{12}\varphi_{13}} = \overline{\varphi_{12}}\,\overline{\varphi_{13}} = \overline{\varphi_{12}}^{\,2}.$$

However, the three functions $\varphi_{12}, \varphi_{13}, \varphi_{23}$ are not mutually independent. Yet one may write

$$\overline{\varphi_{12}\varphi_{13}\varphi_{23}} = \overline{\varphi_{12}}\,\overline{\varphi_{13}}\,\overline{\varphi_{23}} \tag{2}$$

as a first approximation for low density. The rationale is, that this equality would be correct if one of the φ's were replaced with 1; but the configurations for which all three φ's differ from 1 are rare if the density is low.

For products of φ's involving more than three particles a similar argument applies. One is thus led to the first approximation

$$Q_N^{(1)}/V^N = \overline{\varphi_{12}}\,\overline{\varphi_{13}} \dots \overline{\varphi_{N-1,N}} = (\overline{\varphi_{12}})^{\frac{1}{2}N(N-1)}$$

This yields the usual result for the second virial coefficient in the following way.

$$\frac{Q_N^{(1)}}{V^N} = \left[\int e^{-\beta v_{12}} \frac{\mathrm{d}\boldsymbol{r}_1}{V} \frac{\mathrm{d}\boldsymbol{r}_2}{V}\right]^{\frac{1}{2}N(N-1)} = \left[1 + \frac{1}{V}\int \{e^{-\beta v(\boldsymbol{r})} - 1\}\,\mathrm{d}\boldsymbol{r}\right]^{\frac{1}{2}N(N-1)}$$

In the limit of a large system (i.e., $N \to \infty$, $V \to \infty$, $N/V = n =$ constant)

$$\lim \frac{(Q_N^{(1)})^{1/N}}{V} = \exp\,[\tfrac{1}{2}n \int \{e^{-\beta v(\boldsymbol{r})} - 1\}\,\mathrm{d}\boldsymbol{r}] = \exp[\tfrac{1}{2}n\beta_1],$$

where β_1 is Mayer's first irreducible cluster integral [1][2]. Thus

$$Q_N^{(1)} = V^N \exp\left[\frac{N^2}{2V}\,\beta_1\right]. \tag{3}$$

This is the familiar first term in the expansion in powers of the density, which leads to the second virial coefficient. It should be noted that the correct exponential form is obtained without summing over an infinite set of graphs with cumbersome combinatorial factors.

2. *The second approximation* (*order* n^2). The above method of arriving at the second virial coefficient is not new [3]; however, our real problem is to find the higher orders in the expansion. This will be done by supplying successive correction *factors*, rather than additive terms. These correction factors describe successively the statistical correlations between the φ's, which have been neglected in the first approximation.

It is reasonable to expect (and it will be verified by the result) that the next approximation involves three-particle correlations. The triplet of particles 1, 2, 3 gave rise in the first approximation to the factor (2). To make up for the error committed there one has to multiply by the correction factor

$$\frac{\overline{\varphi_{12}\varphi_{13}\varphi_{23}}}{\overline{\varphi_{12}}\,\overline{\varphi_{13}}\,\overline{\varphi_{23}}} = \frac{\overline{\varphi_{12}\varphi_{13}\varphi_{23}}}{\overline{\varphi_{12}}^{3}}.$$

As there are $\binom{N}{3}$ triplets of particles, this factor has to be raised to the power $\binom{N}{3}$. Writing, as usually, $\varphi_{ij} = 1 + f_{ij}$ one finds for the total second order correction factor to Q_N

$$\left[\frac{1 + 3\overline{f_{12}} + 3\overline{f_{12}}^2 + \overline{f_{12}f_{13}f_{23}}}{1 + 3\overline{f_{12}} + 3\overline{f_{12}}^2 + \overline{f_{12}}^3}\right]^{\frac{1}{6}N(N-1)(N-2)}$$

Now $\overline{f_{12}}$ is proportional to V^{-1}, and $\overline{f_{12}f_{13}f_{23}}$ to V^{-2}. Hence the configurational partition function *per particle*, $(Q_N)^{1/N}$, is

$$[1 + V^{-2}\,\overline{f_{12}f_{13}f_{23}} + O(V^{-3})]^{\frac{1}{6}(N-1)(N-2)}.$$

In the limit $N \to \infty$, with constant n, one has, in the familiar notation [1])[2]),

$$\exp[\tfrac{1}{6}n^2\overline{f_{12}f_{13}f_{23}}] = \exp[\tfrac{1}{3}n^2\beta_2].$$

Collecting results, we have found as a second approximation

$$Q_N^{(2)} = V^N \exp\left[\tfrac{1}{2}\frac{N^2}{V}\,\beta_1 + \tfrac{1}{3}\frac{N^3}{V^2}\,\beta_2\right].$$

It should be noted that we were led directly to the *irreducible* cluster integrals β_k, without the detour via the reducible cluster integrals b_k. The reason is that the method enables one to evaluate the canonical partition function itself, without the aid of the grand canonical (or some alternative) formalism.

3. *The total expansion of the partition function.* In order to find the term of degree $k - 1$ in the density n, consider a group of k particles 1, 2, ..., k, and take all factors φ whose subscripts are taken from this group. The correction factor to be computed is

$$\frac{\overline{\varphi_{12}\varphi_{13}\cdots\varphi_{k-1,k}}}{D},$$

where the denominator D is the previous approximation to the same product. Write the numerator in terms of f's and expand

$$\frac{1}{D}\,\overline{(1 + f_{12})(1 + f_{13})\ldots(1 + f_{k-1,k})} = \tag{4}$$

$$= \frac{1}{D}\left\{1 + \overline{f_{12}} + \ldots + \overline{f_{12}f_{13}\ldots f_{k-1,k}}\right\}.$$

The several terms in this expansion may be arranged in *three classes*:

(i) terms involving less than k particles;

(ii) terms that involve all k particles but are reducible (in the sense that they factorize, each factor involving less than k particles);

(iii) irreducible terms involving all k particles.

All terms of the classes (i) and (ii) belong to lower approximations and are therefore also present in D. The terms of class (iii) are necessarily of order $V^{-(k-1)}$. There are also corresponding terms in D, that is, terms made up with the same factors f but erroneously treated as reducible. It is clear that such terms are of order V^{-k} or smaller. In general, each term in D is identical with a term of class (i) or (ii) in the numerator, or else $O(V^{-k})$. Hence (4) becomes

$$1 + \sum_{\{k\}} \overline{f_{12} f_{13}} \ldots + O(V^{-k}), \tag{5}$$

where the summation extends over all irreducible k-particle terms. This is just the usual irreducible cluster integral:

$$\sum_{\{k\}} \overline{f_{12} f_{13}} \ldots = \frac{(k-1)!}{V^{k-1}} \beta_{k-1}. \tag{6}$$

The total correction factor to the configurational partition function per particle, $(Q_N)^{1/N}$, is obtained by raising (4) to the power

$$\frac{1}{N}\binom{N}{k} \to \frac{N^{k-1}}{k!}.$$

The result is

$$\exp\left[\left(\frac{N}{V}\right)^{k-1} \frac{\beta_{k-1}}{k}\right].$$

Combining these correction factors with the first approximation (3) one obtains the familiar result

$$Q_N = V^N \exp\left[N \sum_{k=1}^{\infty} \left(\frac{N}{V}\right)^k \frac{\beta_k}{k+1}\right].$$

4. *The pair correlation function.* The pair correlation function g_{12} is defined by

$$\frac{g_{12}}{V^2} = \frac{1}{Q_N} \int e^{-\beta(v_{12}+v_{13}+\ldots v_{N-1,N})} \, d\boldsymbol{r}_3 \, d\boldsymbol{r}_4 \ldots d\boldsymbol{r}_N. \tag{7}$$

This integral can be evaluated by the same method.

First we denote the two fixed particles by a and b rather than by 1 and 2, to exhibit clearly that they are not involved in the averaging. Second we note that all factors that do not involve both a and b may be discarded, because the normalization of g_{ab} can be found *a posteriori* from the condition *)

$$g_{ab} \to 1 \quad \text{as} \quad |\boldsymbol{r}_a - \boldsymbol{r}_b| \to \infty.$$

Hence we write

$$g_{ab} = \text{const.}\, \varphi_{ab} \, \overline{\varphi_{a1} \ldots \varphi_{aN} \, \varphi_{b1} \ldots \varphi_{bN} \, \varphi_{12} \varphi_{13} \ldots \varphi_{N-1,N}}.$$

*) All terms of order $1/V$ have already been omitted.

Again the *first approximation* is obtained by regarding all factors as statistically independent. In the result the only factor that depends on both a and b is φ_{ab}, so that

$$g_{ab}^{(1)} = \text{const.}\ \varphi_{ab} = e^{-\beta v_{ab}}. \tag{8}$$

The *next approximation* takes into account correlations that arise from one additional particle. These can be accounted for by supplying the correction factor

$$\left[\frac{\overline{\varphi_{a1}\,\varphi_{b1}}}{\overline{\varphi_{a1}}\;\overline{\varphi_{b1}}}\right]^N.$$

Expansion in f's yields

$$\left[\frac{1 + 2\overline{f_{a1}} + \overline{f_{a1}f_{b1}}}{1 + 2\overline{f_{a1}} + \overline{f_{a1}}^2}\right]^N.$$

As both $\overline{f_{a1}}$ and $\overline{f_{a1}f_{b1}}$ are of order V^{-1}, this is equal to

$$\{1 + \overline{f_{a1}f_{b1}} + O(V^{-2})\}^N = \exp\left[\frac{N}{V}\int f_{a1}f_{b1}\,\mathrm{d}\boldsymbol{r}_1\right].$$

Combining this correction factor with (8), one finds the familiar result [4][5][2]

$$g_{ab}^{(2)} = e^{-\beta v_{ab}} \exp\left[\frac{N}{V}\int (e^{-\beta v_{a1}} - 1)\,(e^{-\beta v_{b1}} - 1)\,\mathrm{d}\boldsymbol{r}_1\right].$$

It is readily seen how this process continues step by step. For the k-th correction factor one selects k particles in addition to a and b, and writes the product of all φ's that connect two of these $k + 2$ particles, excepting φ_{ab}.

$$\frac{g_{ab}^{(k+1)}}{g_{ab}^{(k)}} = \left[\frac{\overline{\varphi_{a1}\cdots\varphi_{ak}\varphi_{b1}\cdots\varphi_{bk}\varphi_{12}\cdots\varphi_{k-1,k}}}{D}\right]^{\binom{N}{k}}. \tag{9}$$

On expanding in f's the numerator consists of four classes of terms:

(i) terms involving less than $k + 2$ particles;

(ii) terms that involve all $k + 2$ particles but are reducible, in the sense that a factor can be split off which does not contain a or b;

(iii) irreducible terms involving all $k + 2$ particles, which however decompose in two or more disconnected parts when a and b are erased;

(iv) irreducible terms involving all $k + 2$ particles which remain connected on erasing a and b.

It is clear that the terms of classes (i) and (ii) belong to a lower approximation and therefore also occur in D. Each term of class (iii) decomposes in two or more products which have no other particles in common than a

and b. As a and b are kept fixed while averaging, these terms also decompose in factors with fewer particles, and are therefore also contained in D. In the same way as in section 3 it can be seen that all other terms in D are of order V^{-k-1} or higher. Hence we find for (9)

$$\Big[1 + \sum_{(\mathrm{iv})} \overline{f_{a1} f_{b1} \cdots}\Big]^{N^k/k!},$$

where the summation extends over all terms of class (iv).

The terms of class (iv) are averaged over k particles and are therefore proportional to V^{-k}. In the notation of Mayer and Montroll *)

$$\sum_{(\mathrm{iv})} \overline{f_{a1}\, f_{b1} \cdots} = \frac{1}{k!V^k}\, h_{2,k}(a, b).$$

Hence the correction factor (9) becomes

$$\exp\Big[\Big(\frac{N}{V}\Big)^k h_{2,k}(a, b)\Big].$$

Combining these correction factors with the first approximation (8) one obtains the known result [5])

$$g_{ab} = e^{-\beta v_{ab}} \exp\Big[\sum_{k=1}^{\infty} \Big(\frac{N}{V}\Big)^k h_{2,k}(a, b)\Big]. \tag{10}$$

This may also be described in terms of a "potential of mean force"

$$W(\boldsymbol{r}_a, \boldsymbol{r}_b) = v_{ab} - \kappa T \sum_{k=1}^{\infty} n^k h_{2,k}(a, b).$$

It is clear that the method can be extended without much trouble to correlation functions for more than two particles.

5. *The partition function in an external field.* The same method can be used to compute the configurational partition function in an external field $u(\boldsymbol{r})$,

$$Q_N^* = V^N \overline{\psi_1 \psi_2 \ldots \psi_N}\ \overline{\varphi_{12}\, \varphi_{13} \ldots \varphi_{N-1,N}}\,, \tag{11}$$

where $\psi_i = e^{-\beta u(\boldsymbol{r}_i)}$.

Again a first approximation is obtained by regarding all factors as statistically independent.

$$\begin{aligned} Q_N^{*(1)} &= V^N\, \overline{\psi_1}^N (\overline{\varphi_{12}})^{\frac{1}{2}N(N-1)} \\ &= Q_N^{(1)}\, \overline{\psi_1}^N. \end{aligned}$$

*) Class (iv) is defined by Mayer and Montroll as follows: "all connected products in which the vertices 1, 2, ..., k are connected independently of a, b, and each of them is connected by independent paths to a and b". According to Menger's theorem [6]) this last clause is equivalent with our exclusion of reducible terms (as defined under class (ii)).

In the next approximation correlations between two particles have to be taken into account. The new correction factor is

$$\left[\frac{\overline{\psi_1\psi_2\varphi_{12}}}{\overline{\psi_1}^2\,\overline{\varphi_{12}}}\right]^{\frac{1}{2}N(N-1)}.$$

A calculation along the same lines as before shows that this is equal to

$$\exp\left[\frac{N^2}{2\overline{\psi_1}^2 V}\int(\psi_1\psi_2-\overline{\psi_1}^2)\,f_{12}\frac{\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2}{V}\right]. \tag{12}$$

There is, however, an alternative method for computing Q_N^*, which is very convenient for obtaining a general expansion. We define a new averaging process (distinguished from the previous one by an asterisk) as follows. For any function χ_1 of the coordinates of particle 1 we write

$$\overline{\chi_1}^* = \frac{\int \chi_1\psi_1\,\mathrm{d}\boldsymbol{r}_1}{\int\psi_1\,\mathrm{d}\boldsymbol{r}_1} = \frac{\overline{\chi_1\psi_1}}{\overline{\psi_1}}. \tag{13}$$

Moreover it is convenient to put

$$V^* \equiv \int\psi_1\,\mathrm{d}\boldsymbol{r}_1 = V\overline{\psi_1}.$$

The definition of this average for more particles is obvious. Equation (11) may now be written

$$Q_N^* = (V^*)^N\,\overline{\varphi_{12}\varphi_{13}\cdots\varphi_{N-1,N}}^*,$$

in complete analogy with (1).

The calculation of Q_N^* can now be copied from the calculation of Q_N in section 3. The result is

$$Q_N^* = V^{*N}\exp\left[N\sum_{k=1}^{\infty}\left(\frac{N}{V^*}\right)^k\frac{\beta_k^*}{k+1}\right], \tag{14}$$

where the β_k^* are defined, in analogy (6), by

$$\frac{(k-1)!}{(V^*)^{k-1}}\beta_{k-1}^* = \sum_{\{k\}}\overline{f_{12}f_{13}\cdots}^*, \tag{15}$$

the summation extending again over all irreducible k-particle terms. The first term in (14) is identical with the approximation (12).

The result (14) can be employed for an alternative calculation of the pair-distribution function. Indeed, according to the definition (7) one has

$$\frac{g_{ab}}{V^2} = e^{-\beta v_{ab}}\frac{Q_{N-2}^*}{Q_N},$$

where Q_{N-2}^* is the partition function of the remaining $N-2$ particles in the field caused by a and b. From this identity follows

$$g_{ab} = e^{-\beta v_{ab}}\, V^2 \frac{Q_{N-2}}{Q_N} \frac{Q_N^*}{Q_N}$$

$$= e^{-\beta v_{ab}} \left(\frac{V^*}{V}\right)^N \exp\left[-2 \sum_{k=1}^{\infty} \left(\frac{N}{V}\right)^k \beta_k\right] \exp\left[\sum_{k=1}^{\infty} \frac{N^{k+1}}{k+1} \left(\frac{\beta_k^*}{V^{*k}} - \frac{\beta_k}{V^k}\right)\right]. \tag{16}$$

Because of the special form of the external field,

$$\frac{V^*}{V} = \overline{\psi_1} = \overline{\varphi_{a1}\varphi_{b1}} = 1 + \frac{2}{V}\beta_1 + \frac{1}{V} h_{2,1}(a, b). \tag{17}$$

Hence

$$\left(\frac{V^*}{V}\right)^N = \exp\left[\frac{2N}{V}\beta_1 + \frac{N}{V} h_{2,1}(a, b)\right].$$

Substitute this in (16) and rearrange terms:

$$g_{ab} = e^{-\beta v_{ab}} \exp\left[\frac{N}{V} h_{2,1}\,(a, b)\right] \times$$

$$\times \exp\left[\sum_{k=2}^{\infty} \left(\frac{N}{V}\right)^k \left\{\frac{V}{k}\left(\frac{\beta_{k-1}^*}{\overline{\psi_1}^{k-1}} - \beta_{k-1}\right) - 2\beta_k\right\}\right]. \tag{18}$$

It is shown in appendix II that this result is identical with the usual formula (10).

Appendix I. *Explicit verification of the third approximation.* Consider the particles 1, 2, 3, 4; the factor to be computed is

$$\overline{\varphi_{12}\varphi_{13}\varphi_{14}\varphi_{23}\varphi_{24}\varphi_{34}}. \tag{19}$$

This factor can be represented by the graph in fig. 1. The *first* approximation is

$$\overline{\varphi_{12}}\;\overline{\varphi_{13}}\;\overline{\varphi_{14}}\;\overline{\varphi_{23}}\;\overline{\varphi_{24}}\;\overline{\varphi_{34}} = \overline{\varphi_{12}}^6.$$

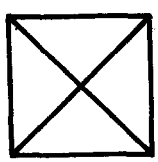

Fig. 1. The graph for the φ's.

In *second* approximation this was corrected by the factor

$$\left[\frac{\overline{\varphi_{12}\varphi_{13}\varphi_{23}}}{\overline{\varphi_{12}}^3}\right]^4;$$

the exponent 4 is due to the fact that there are four ways of selecting a triplet from the six φ's in (19). Hence the second approximation to (19) is

$$\frac{(\overline{\varphi_{12}\varphi_{13}\varphi_{23}})^4}{\overline{\varphi_{12}}^6}.$$

The *third* approximation therefore adds the correction factor

$$\frac{\overline{\varphi_{12}}^6\,\overline{\varphi_{12}\varphi_{13}\varphi_{14}\varphi_{23}\varphi_{24}\varphi_{34}}}{(\overline{\varphi_{12}\varphi_{13}\varphi_{23}})^4}.$$

Expanding in the f's and omitting all terms of order V^{-4} or higher, one finds

$$\overline{\varphi_{12}}^6 = 1 + 6\,\overline{f_{12}} + 15\,\overline{f_{12}}^2 + 20\,\overline{f_{12}}^3. \tag{20}$$

$$\begin{aligned}(19) = 1 &+ 6\,\overline{f_{12}} + 15\,\overline{f_{12}}^2 + 16\,\overline{f_{12}}^3.\\ &+ 4\,\overline{f_{12}f_{13}f_{23}} + 12\,\overline{f_{12}}\cdot\overline{f_{12}f_{13}f_{23}}\\ &+ 3\,\overline{f_{12}f_{14}f_{23}f_{34}} + 6\,\overline{f_{12}f_{13}f_{14}f_{23}f_{34}}\\ &+ \overline{f_{12}f_{13}f_{14}f_{23}f_{24}f_{34}}.\end{aligned} \tag{21}$$

$$\begin{aligned}(\overline{\varphi_{21}\varphi_{13}\varphi_{23}})^4 = 1 &+ 12\,\overline{f_{12}} + 66\,\overline{f_{12}}^2 + 216\,\overline{f_{12}}^3\\ &+ 4\,\overline{f_{12}f_{13}f_{23}} + 36\,\overline{f_{12}}\cdot\overline{f_{12}f_{13}f_{23}}.\end{aligned} \tag{22}$$

Multiplying (20) and (21) one easily verifies that all terms of order V^{-1} or V^{-2} are identical with those of (22); and that the terms of order V^{-3} are also identical, but for the last three in (21). They correspond to the three irreducible diagrams of fig. 2 successively, and together they make up the desired term

$$3!\,V^{-3}\beta_3.$$

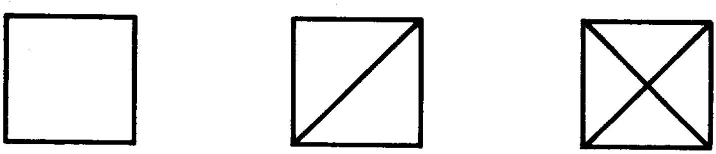

Fig. 2. The graphs for the f's.

Appendix II. *Proof that* (10) *and* (16) *are identical.* We have to prove that

$$h_{2,k}(a, b) = \frac{V}{k}\left(\frac{\beta^*_{k-1}}{\overline{\psi_1}^{k-1}} - \beta_{k-1}\right) - 2\beta_k \tag{23}$$

for $k = 2, 3, \ldots$. According to the definitions (15) and (13)

$$\beta^*_{k-1} = \frac{V^{k-1}}{(k-1)!\,\overline{\psi_1}} \sum_{\{k\}} \overline{f_{12} \cdots \varphi_{a1}\varphi_{b1} \cdots \varphi_{ak}\varphi_{bk}}.$$

If one writes $\varphi_{a1} = 1 + f_{a1}$, etc., this takes the form

$$\beta^*_{k-1} = \frac{V^{k-1}}{(k-1)!\,\overline{\psi_1}} \sum_{\{k\};a,b} \overline{f_{12}\ldots},$$

the summation extending over all graphs which connect the particles 1, 2, ..., k in an irreducible fashion and are connected by any number (from zero to $2k$) of lines with a and b.

The contribution to β^*_{k-1} of those graphs that are not connected with a or b is $(\overline{\psi_1})^{-1}\beta_{k-1}$. All other contributions are proportional to V^{-k}. Hence the right-hand side of (23) is, apart from terms $O(V^{-1})$,

$$\frac{V}{k}\left(\frac{1}{\overline{\psi_1}} - 1\right)\beta_{k-1} + \frac{V^k}{k!} \sum_{\{k\};a,b}{}' \overline{f_{12}\ldots} - 2\frac{V^k}{k!} \sum_{\{k+1\}} \overline{f_{12}\ldots}\,. \tag{24}$$

The first term is equal to (compare (17))

$$\frac{V}{k}\left(-\frac{2k}{V}\beta_1 - \frac{k}{V}h_{2,1}\right)\beta_{k-1} + O(V^{-1}). \tag{25}$$

The second term contains the contributions of the following four types of graphs.

(i) Irreducible k-graphs linked *once* with either a or b. Each of them contributes to this term

$$\frac{V^k}{k!}\cdot\beta_1\cdot\frac{(k-1)!}{V^k}\beta_{k-1} = \frac{\beta_1\beta_{k-1}}{k}\,.$$

As there are $2k$ of such graphs, their contributions exactly cancel the first term of (25).

(ii) Irreducible k-graphs of which *one* vertex is linked with *a and b*. It is easily seen that they cancel the second term of (25).

(iii) Irreducible k-graphs of which *two or more* vertices are linked with a and none with b (or vice versa). These are the irreducible $(k+1)$-graphs; their contributions cancel the last term in (24).

(iv) The remaining graphs are just the ones that make up $h_{2,k}(a, b)$ — which proves the identity (23).

Received: 6-5-61

REFERENCES

1) Mayer, J. E. and Mayer, M. G., *Statistical Mechanics* (New York 1940).
2) De Boer, J., Rep. Prog. Phys. **12** (1948/1949) 305; Münster, A., *Statistische Thermodynamik* (Berlin 1956); Mayer, J. E., Handb. Physik **12**, 73 (Berlin 1958).
3) Landau, L. D. and Lifshitz, E. M., *Statistical Physics* (English translation, London 1958) p. 220; Brout, R., Proc. Intern. Cong. Many-Particle Problems, Utrecht 1960 (Physica **26**, 1960, Supp.) page S 28. Brout also finds the higher terms by expanding in powers of β and summing ladder graphs.
4) De Boer, J. and Michels, A., Physica **6** (1939) 97.
5) Mayer, J. E. and Montroll, E., J. chem. Phys. **9** (1941) 2.
6) König, D., *Theorie der endlichen und unendlichen Graphen* (Leipzig 1936; New York 1950) page 244.