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Theory of Classical Fluids: Hyper-Netted Chain Approximation. III

——*A New Integral Equation for the Pair Distribution Function*——

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The hyper-netted chain approximation proposed in I is reformulated. The formulae in this approximation are rederived for the free energy, chemical potential and pair distribution function. The pair distribution function in our approximation is shown to satisfy a new integral equation, which is compared with the Yvon, Born and Green one. Variational principle for our approximation is given.

Errata for I and II are given as appendix.

§ 1. Introduction

The HNC (hyper-netted chain) approximation is proposed in I,[1] so that we may theoretically approach to the behaviors of fluids of not too small densities by starting with the Mayer virial expansion formulae. In this approximation, we try to consider all the graphs which can be summed up by means of sequences of the Fourier transformation. These graphs are considered to be those which can be reduced to a line or a ring by a sequence of 'identifications'.* In I, we have grouped the graphs by the 'times of identifications'* by which a graph is reduced to a line or a ring. The author regrets the fact that he committed errors in the calculations in I and II,[2] in which some graphs which should have been included were neglected. The errata for I and II will be given in the Appendix. The correct results were reported in the preliminary report.[3]

In this paper, we will reformulate the hyper-netted chain approximation in a more refined form than in I.

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* The terminology will follow that in I. Some important words to be explained are as follows:

A 'propagation' is a part of graph which is connected to another part of the graph by just two points. The corresponding factor is called 'propagator'.

A 'junction' is a point where three or more lines meet.

Two or more propagations with the same endpoints are called 'identifiable' if they have no junctions midway. 'Identification' is the process of replacing two or more identifiable propagations by a line.

'Times of identification' are counted by carrying identifications on every identifiable parts on a graph at the same time.

The notation is somewhat changed. $f^{(0)}(r)$, $F^{(0)}(k)$, $\mathfrak{f}(r)$, $\mathfrak{F}(k)$, $\mathfrak{h}(r)$, and $\mathfrak{H}(k)$ in I are written as $b(r)$, $B(k)$, $z(r)$, $Z(k)$, $z_S(r)$ and $Z_S(k)$, respectively, in this paper.

The Mayer virial expansion formulae in which we are interested are as follows:

1a. The free energy A :[4]

$$\frac{A}{VkT}=\rho\ln\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\frac{\rho}{e}+\frac{A'}{VkT}, \tag{1}$$

$$-\frac{A'}{kT}=\frac{\rho^2}{2}\iint d\boldsymbol{r}_1 d\boldsymbol{r}_2 b_{12}+\sum_{n=3}^{\infty}\frac{\rho^n}{n!}\iint\cdots\int d\boldsymbol{r}_1\cdots d\boldsymbol{r}_n\sum_{n\geq i>j\geq 1}\Pi\, b_{ij}. \tag{2}$$

Sum over all products which are more than singly connected.

1b. The chemical potential μ :*

$$\frac{\mu}{kT}=\ln\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\rho+\frac{\mu'}{kT}, \tag{3}$$

$$-\frac{\mu'}{kT}=\rho\int d\boldsymbol{r}_2 b_{12}+\sum_{k=2}^{\infty}\frac{\rho^k}{k!}\iint\cdots\int d\boldsymbol{r}_2\cdots d\boldsymbol{r}_{k+1}\sum_{\substack{k+1\geq i>j\geq 2\\ k+1\geq l\geq 2}}\Pi\, b_{ij}b_{l1}. \tag{4}$$

Sum over all products for which each particle of the set $\{\boldsymbol{r}_2, \cdots, \boldsymbol{r}_{k+1}\}$ is connected to $\boldsymbol{r}_1$ by at least two independent paths and also the particles $\{\boldsymbol{r}_2, \cdots, \boldsymbol{r}_{k+1}\}$ are connected with each other independently of $\boldsymbol{r}_1$.

1c. The pair distribution function $g(r)$ or the potential of average force $\ln g(r)$:[5]

$$\ln g(r)=-\frac{\phi(r)}{kT}+w(r), \tag{5}$$

$$w(r_{12})=\sum_{m=1}^{\infty}\frac{\rho^m}{m!}\iint\cdots\int d\boldsymbol{r}_3\cdots d\boldsymbol{r}_{m+2}\sum_{\substack{m+2\geq i>j\geq 3\\ m+2\geq k\geq 3\\ 2\geq \kappa\geq 1}}\Pi\, b_{ij}b_{k\kappa}, \tag{6}$$

Sum over all products for which each particle of the set $\{\boldsymbol{r}_3, \cdots, \boldsymbol{r}_{m+2}\}$ is connected $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ by an independent path and also the particles $\{\boldsymbol{r}_3, \cdots, \boldsymbol{r}_{m+2}\}$ are connected with each other independently of $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$.

where

$$b_{ij}=b(r_{ij})=\exp\{-\phi(r_{ij})/kT\}-1,$$

$\phi(r)$ being the intermolecular potential.

Mayer[4] introduced graphs to illustrate the integrals in the sums of the right-hand side of (2), (4) and (6). In our development, it is convenient to use the graphical representation of the integrands and integral of (2), (4) and (6) systematically. So we use the graphs as the symbols for products or integrals. We start with definition of the symbolical representations in § 2 and go forth with the thorough use of the symbolical methods.

In § 3 the hyper-netted chains which satisfy a set of equations are defined. In § 4 the formulae for the free energy, chemical potential and pair distribution function in terms of the hyper-netted chains are obtained in the HNC approxima-

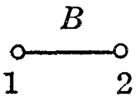
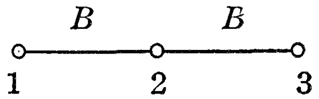
* $-\mu'/kT$ is equal to $-\ln\gamma=\sum_{k=1}^{\infty}\beta_k\rho^k$ in Mayer's textbook.[4]

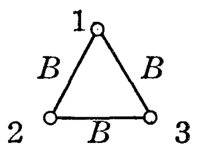
tion. The expansion formulae for the free energy, chemical potential and pair distribution function in terms of the hyper-netted chains are given in § 5. The variational principle for the free energy in the HNC approximation is given in § 6. By using this variational principle, we calculate in § 7 the expressions for the pressure and internal energy in the HNC approximation. The set of equations for the pair distribution function in the HNC approximation is compared with that of Yvon, Born and Green in § 8.

Discussions are given only for a one-component system.

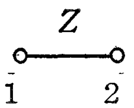
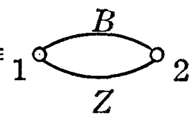
§ 2. Definitions of graphs

2a. Product $\prod_{n\geq i>j\geq 1} b_{ij}$ is expressed by a graph which consists of n white circles with subscripts $1, 2, \cdots, n$; $\circ_1, \circ_2, \cdots, \circ_n$; and lines connecting $\circ_i$ and $\circ_j$ corresponding to the appearance of factors b_{ij} in the product, where the line is attached by letter B, specifying that the factor is $b(r)$. In case where another factor appears, a corresponding letter will be attached. For instance,

$b_{12} \equiv$  , $b_{12}b_{23} \equiv$  ,

$b_{12}b_{13}b_{23} \equiv$ 

and

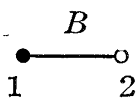
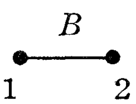
$z_{12} \equiv$  , $b_{12}z_{12} \equiv$  ,

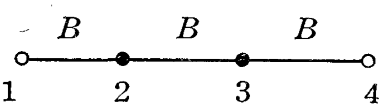
and so on.

2b. In order to express the integrals in (2), (4) and (6), we introduce a symbol expressing

$$\rho^m \iint \cdots \int d\boldsymbol{r}_{n-m+1} \cdots d\boldsymbol{r}_n \prod_{n\geq i>j\geq 1} b_{ij}.$$

It is the graph obtained from the graph expressing $\prod_{n\geq i>j\geq 1} b_{ij}$ by replacing the white circles $\circ_{n-m+1}, \cdots, \circ_n$ by the black circles $\bullet_{n-m+1}, \cdots, \bullet_n$: a black circle means that an integration is to be taken over the coordinate. For instance,

$\rho \int d\boldsymbol{r}_1 b_{12} \equiv$  , $\rho^2 \iint d\boldsymbol{r}_1 d\boldsymbol{r}_2 b_{12} \equiv$  ,

$\rho^2 \iint d\boldsymbol{r}_2 d\boldsymbol{r}_3 b_{12} b_{23} b_{34} \equiv$  , and so on.

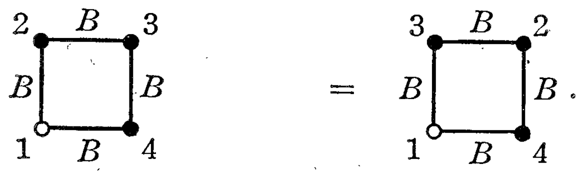
Now, we write the formulae (2), (4) and (6) as follows:

$$-A'/kT=\frac{1}{2}\ \underset{1}{\bullet}\!\overset{B}{\text{——}}\!\underset{2}{\bullet}\ +\sum_{n=3}^{\infty}\frac{1}{n!}$$ {*Sum of all the topologically different graphs which consist of* $\bullet_1$, $\bullet_2$, $\cdots$, $\bullet_n$ *and some* $\overset{B}{\text{——}}$ *and which are more than singly connected.*} (2′)

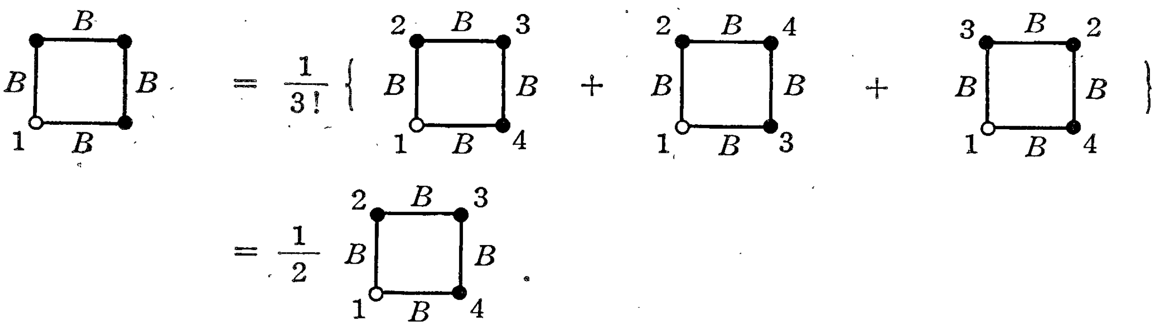
$$-\mu'/kT=\underset{1}{\circ}\!\overset{B}{\text{——}}\!\underset{2}{\bullet}\ +\sum_{k=2}^{\infty}\frac{1}{k!}$$ {*Sum of all the topologically different graphs which consist of* $\circ_1$, $\bullet_2$, $\bullet_3$, $\cdots$, $\bullet_{k+1}$ *and some* $\overset{B}{\text{——}}$ *and for which each black circle is connected to* $\circ_1$ *by at least two independent paths and the black circles are connected to each other independently of* $\circ_1$*.*} (4′)

$$w(r_{12})=\sum_{m=1}^{\infty}\frac{1}{m!}$$ {*Sum of all the topologically different graphs which consist of* $\circ_1$, $\circ_2$, $\bullet_3$, $\bullet_4$, $\cdots$, $\bullet_{m+2}$ *and some* $\overset{B}{\text{——}}$ *and in which each black circle is connected to* $\circ_1$ *and* $\circ_2$ *by an independent path and the black circles are connected to each other independently of* $\circ_1$ *and* $\circ_2$; *where* $\overset{B}{\text{——}}$ *directly connecting* $\circ_1$ *and* $\circ_2$ *is not allowed.*} (6′)

2c. In the sums in (2′), (4′) and (6′) appear many graphs which are different only in the numbers attached to the black circles: they are, of course, of the same contributions to (2′), (4′) and (6′); e.g.,



We now define the graph with black circles without subscripts. It represents the sum of the graphs, with black circles with subscripts, which are topologically different from each other only in the numbering of the black circles, divided by the factorial of the number of the black circles. So that, e.g.,



Then, (2′), (4′) and (6′) are written in terms of these graphs as

$-A'/kT=$ $\bullet\overset{B}{\text{——}}\bullet$ *+Sum of all the topologically different graphs which consist of three or more black circles without subscript and some* $\overset{B}{\text{——}}$ *and which are more than singly connected.* (2″)

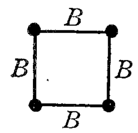
$-\mu'/kT=$ $\circ\overset{B}{\text{——}}\bullet$ *+Sum of all the topologically different graphs which consist of one white circle and two or more black circles without subscript and some* $\overset{B}{\text{——}}$ *and for which each black circle is connected to the white circle by at least two independent paths and the black circles are connected to each other independently of the white circle.* (4″)

$w(r_{12})$ *=Sum of all the topologically different graphs which consist of two white circles* $\bigcirc_1$ *and* $\bigcirc_2$ *and one or more black circles and some* $\overset{B}{\text{——}}$ *and for which each black circle is connected to* $\bigcirc_1$ *and* $\bigcirc_2$ *by an independent path and the black circles are connected to each other independently of* $\bigcirc_1$ *and* $\bigcirc_2$, *where* $\overset{B}{\text{——}}$ *directly connecting* $\bigcirc_1$ *and* $\bigcirc_2$ *is not allowed.* (6″)

Given a graph with black circles with subscript, the number of corresponding graphs topologically different only in the numbering of the black circles is equal to the factorial of the number of black circles in the graph divided by the number of symmetry of the corresponding graph with black circles without subscript. As the consequence, a graph with black circles without subscript expresses an integral of the type:

$$\frac{\rho^m}{\text{The number of symmetry of the graph with black circles without subscript.}}\cdot\iint\cdots\int d\boldsymbol{r}_{n-m+1}\cdots d\boldsymbol{r}_n \prod_{n\geq i>j\geq 1} b_{ij}.$$

That is, e.g.,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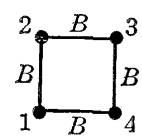
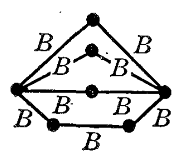
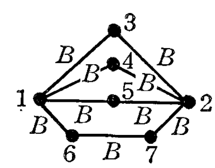
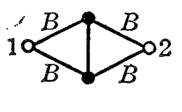
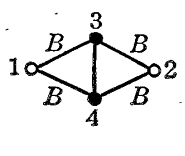



$=\dfrac{1}{2\times 3!}$



$=\dfrac{1}{2}$


and so on.

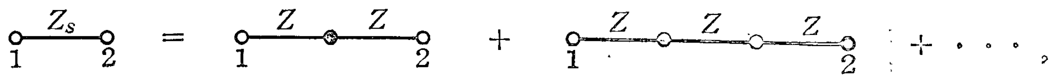
§ 3. The hyper-netted chains

The hyper-netted chain approximation is introduced as the approximation in which all those graphs are considered, which are reducible to a line by a sequence of identifications. Then, these graphs are considered to be constructed of propagations which are reducible to a line by identifications. We group these propagations into two classes, which will be called 'hyper-netted chain Z' and 'hyper-netted chain Z_S'. To define these, we define an 's-point' as a point which must be passed to go from an end of a propagation to another end.

The hyper-netted chain Z is the total of the propagations which are reducible to a line by identifications and which have no s-point. The corresponding propagators are $z(r)$ and $Z(k)$.*

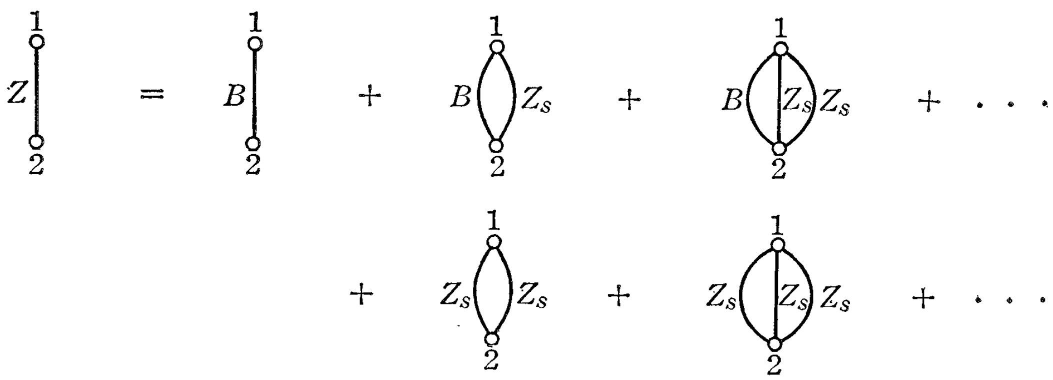
The hyper-netted chain Z_S is the total of the propagations which are reducible to a line by identifications and which have at least one s-point. The corresponding propagators are $z_S(r)$ and $Z_S(k)$.

According to the definitions, the structure of Z and Z_S are of the form:



(7f)

where we have grouped the graphs in Z_S together according to the number of s-points, and



(8f)

where we have grouped the graphs in Z together according to the number of propagations in which the propagation separates when we erase the endpoints. $Z\Big|^{\circ 1}_{\circ 2}$ is the sum of all topologically different graphs of the type of (8f) and each graph is equal to a graph with black circles with subscript divided by the number

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* $Z(k)$ and $Z_S(k)$ are Fourier transforms of $z(r)$ and $z_S(r)$, respectively. That is, e. g.,

$$Z(k)=\int d\boldsymbol{r}\, z(r) \exp (i\boldsymbol{k}\cdot\boldsymbol{r}) .$$

of symmetry. *The number of symmetry is equal to the product of the numbers of symmetry of each edge and the number of symmetry of the graph as a whole.* Then (8f) can be written as

$$Z\underset{2}{\overset{1}{\Big|}} = \left\{B\underset{2}{\overset{1}{\Big|}} + 1\right\} \sum_{n=1}^{\infty} \sum_{\substack{Z_S' < Z_S'' < \cdots < Z_S^{(l)} ** \\ n = n'+n''+\cdots+n^{(l)}}} \sum \cdots \sum \frac{1}{n'!}\left\{\underset{2}{\overset{1}{\Big|}}Z_S'\right\}^{n'} \cdot \frac{1}{n''!}\left\{\underset{2}{\overset{1}{\Big|}}Z_S''\right\}^{n''} \cdots \frac{1}{n^{(l)}!}\left\{\underset{2}{\overset{1}{\Big|}}Z_S^{(l)}\right\}^{n^{(l)}}$$

$$+B\underset{2}{\overset{1}{\Big|}} - Z_S\underset{2}{\overset{1}{\Big|}}$$

$$= \left\{B\underset{2}{\overset{1}{\Big|}} + 1\right\} \sum_{n=1}^{\infty} \frac{1}{n!}\left\{\sum_{Z'_S} \underset{2}{\overset{1}{\Big|}}Z_S'\right\}^{n} + B\underset{2}{\overset{1}{\Big|}} - Z_S\underset{2}{\overset{1}{\Big|}}$$

$$= \left\{B\underset{2}{\overset{1}{\Big|}} + 1\right\} \sum_{n=1}^{\infty} \frac{1}{n!}\left\{\underset{2}{\overset{1}{\Big|}}Z_S\right\}^{n} + B\underset{2}{\overset{1}{\Big|}} - Z_S\underset{2}{\overset{1}{\Big|}}, \tag{8f'}$$

so that

$$z(r) = \{b(r) + 1\} e^{z_S(r)} - 1 - z_S(r). \tag{8}$$

In the graphical equation (8f′), Z_S', Z_S'', $\cdots$, $Z_S^{(l)}$ means a graph belonging to the hyper-netted chain Z_S. Note here that the inverse of the number of symmetry of each edge is included in the respective $\underset{2}{\overset{1}{\Big|}}Z_S'$ On the other hand, (7f) is in its explicit form,

$$Z_S(k) = \frac{\rho Z(k)^2}{1 - \rho Z(k)}. \tag{7}$$

This set of equations, (7) and (8), determines $z(r)$ and $z_S(r)$.

§ 4. Formulae in the HNC approximation

We calculate the sums of the graphs which are reducible to a line or a ring by identifications, in (2″), (4″) and (6″). We consider first (6″) and then (4″) and (2″).

4a. The potential of average force

The total of the graphs which connect $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ and which can be reduced to a line by identifications are Z and Z_S. In (6″), we have only to consider the

* The inequalities mean that the sum is taken over all those sets $\{Z_S', Z_S'', \ldots, Z_S^{(l)}\}$ for which $Z_S', \ldots, Z_S^{(l)}$ are different from each other, in the way as to consider every set only once.

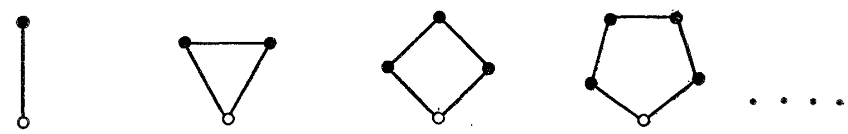
graphs in which the black circles are connected independently of $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. The graphs in Z are not of such nature. The graphs to be considered are those of Z_S and we get

$$w(r)_{HNC}=z_S(r). \tag{9}$$

Now, we note that the set of equations (7) and (8) is just the set of equations which determines the pair distribution function in the HNC approximation.

4b. The chemical potential

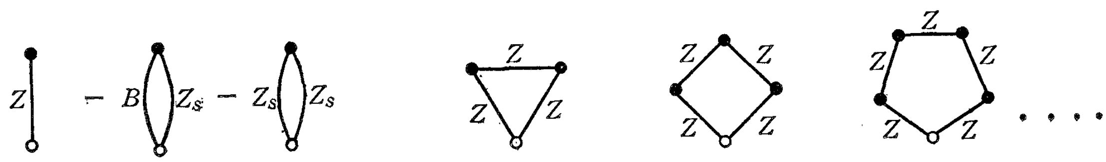
After a sequence of identifications except the point $\boldsymbol{r}_1$, any graph which is reducible to a line or a ring is reduced to one of the graphs in Fig. 1.



1a 1b 1c 1d

Fig. 1.

The graphs which are reduced to the form of Figs. 1*a*, 1*b*, 1*c*, $\cdots$ by identifications have the structure of Figs. 2*a*, 2*b*, 2*c*, $\cdots$, respectively. (While the converse is not true.) Then, the contribution to be calculated is the sum of the contri-



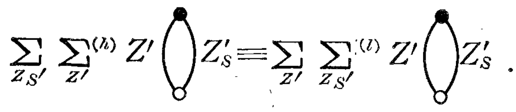
2a 2b 2c 2d

Fig. 2

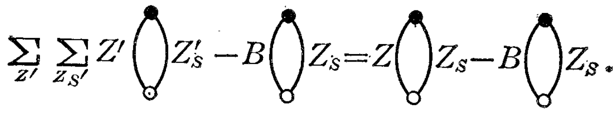
butions of graphs in Figs. 2*a*, 2*b*, 2*c*, $\cdots$, subtracted by the contributions of the graphs which are not reduced to Figs. 1*a*, 1*b*, $\cdots$ among those of Figs. 2*a*, 2*b*, $\cdots$, respectively. These graphs to be subtracted in Fig. 2*a* are those in which the times of identification to reduce to a line are larger for one of Z_S constructing Z than for the other Z_S (cf. (8f)), i.e.,

$$\sum_{Z'}\sum_{Z_S'}{}^{(h+s)} Z'\bigcirc Z_S' - B\bigcirc Z_S\,.$$

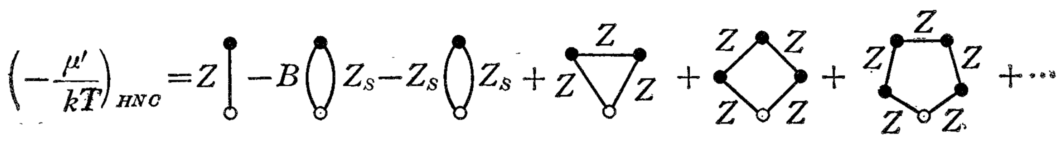
Here, $\sum_{Z_S'}{}^{(h+s)}$ means that the sum over is taken over Z_S' for which the times of identification to reduce to a line is the same or larger than Z' in the first sum; Z' | means a graph belonging to the set Z |. Such graphs in Figs. 2*b*, 2*c*, $\cdots$, are those in which the times of identification to reduce to a line is larger for an edge Z attached to $\boldsymbol{r}_1$ than the other edges of Z_S, that is

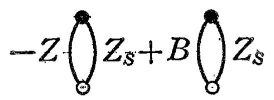


Here, (l) on $\sum_{Z_S'}^{(l)}$ means the lower; cf. above $\sum_{Z_S'}^{(h+s)}$. As the consequence, the contribution to be subtracted is



Then, the contribution to be calculated is





(10 f)

or explicitly

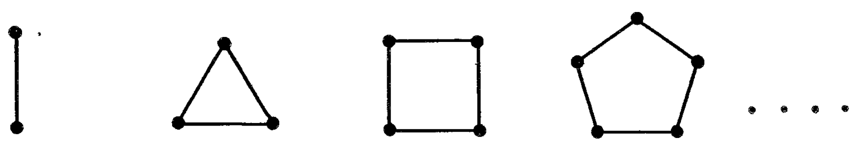
$$\left(-\frac{\mu'}{kT}\right)_{HNC}=\int d\boldsymbol{r}\left\{\rho z(r)-\rho b(r)z_S(r)-\frac{\rho}{2}z_S(r)^2\right\}+\frac{1}{2}\left\{z_S(0)-\rho\int d\boldsymbol{r}\,z(r)^2\right\}$$

$$-\int d\boldsymbol{r}\left\{\rho z(r)z_S(r)-\rho b(r)z_S(r)\right\}$$

$$=\rho Z(0)+\frac{1}{2}z_S(0)-\frac{\rho}{2}\int d\boldsymbol{r}\left\{z(r)+z_S(r)\right\}^2. \tag{10}$$

4c. The free energy

After a sequence of identifications, any of the graphs to be considered is reduced to one of the forms in Fig. 3. The graphs which reduce to the form of Figs.



3a 3b 3c 3d

Fig. 3.

$3a$, $3b$, $3c$, $\cdots$, by identifications have the structure of Figs. $4a$, $4b$, $4c$, $\cdots$, respectively. (While the converse is not true again.) Then, the contribution to be calculated is the sum of the contributions of Figs. $4a$, $4b$, $4c$, $\cdots$, subtracted by the

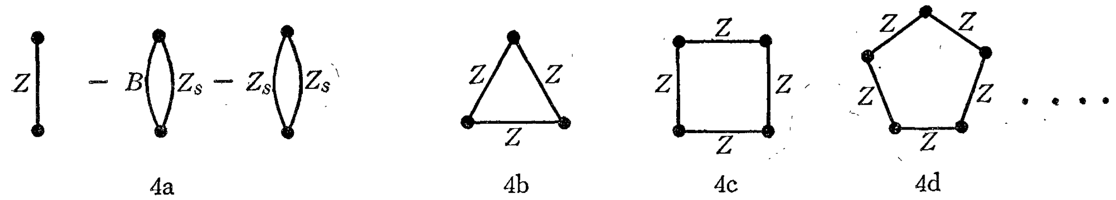


Fig. 4.

contributions of the graphs which do not reduce to Figs. $3a$, $3b$, $3c$, $\cdots$, among those of Figs. $4a$, $4b$, $4c$, $\cdots$, respectively. These graphs in Fig. $4a$ are those in which the times of identification to reduce to a line is larger for one of Z_S constructing Z than for the other Z_S (cf. Eq. (8f)), that is,

$$\sum_{Z'}\sum_{Z_S'}{}^{(h+s)} Z'\bigcirc Z_S' - Z_S\bigcirc B\,,$$

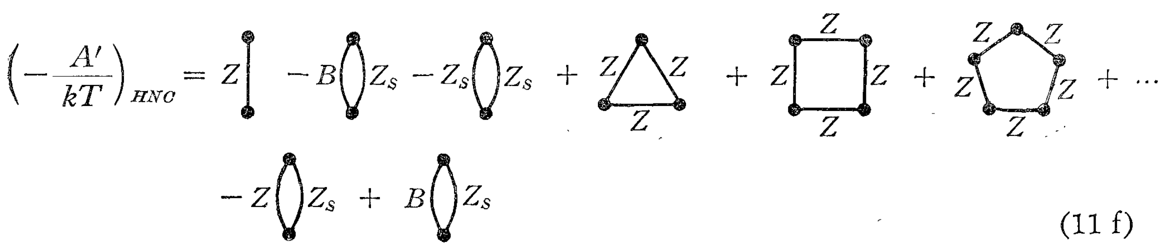
where $Z'\,\overset{\circ}{\underset{\circ}{|}}$ means a graph belonging to $Z\,\overset{\circ}{\underset{\circ}{|}}$. These graphs in Figs. $4b$, $4c$, $\cdots$, are those in which the times of identification to reduce to a line is larger for an edge Z than the other edges. That is,

$$\sum_{Z_S'}\sum_{Z'}{}^{(h)} Z'\bigcirc Z_S' = \sum_{Z'}\sum_{Z_S'}{}^{(l)} Z'\bigcirc Z_S'.$$

Then, the contribution to be subtracted is from the graph:

$$\sum_{Z'}\sum_{Z_S'} Z'\bigcirc Z_S' - Z_S\bigcirc B = Z\bigcirc Z_S - Z_S\bigcirc B.$$

As the consequence, the contribution to be calculated is



or explicitly

$$\left(-\frac{A'}{VkT}\right)_{HNC} = \frac{\rho^2}{2}Z(0) + \frac{1}{2V}\sum_k\left\{-\ln(1-\rho Z(k)) - \rho Z(k) - \frac{1}{2}\rho^2 Z(k)^2\right\}$$
$$-\frac{\rho^2}{4}\int d\boldsymbol{r}\, z_S(r)^2 - \frac{\rho^2}{2}\int d\boldsymbol{r}\, z(r)\, z_S(r)$$
$$= \frac{\rho^2}{2}Z(0) + \frac{1}{2V}\sum_k\left\{-\ln(1-\rho Z(k)) - \rho Z(k) - \frac{\rho^2}{2}[Z(k)+Z_S(k)]^2\right\}. \quad (11)$$

§ 5. Expansion formulae in terms of the hyper-netted chains*

In the previous section, we have summed up the contribution of the graphs which can be reduced to a line or a ring by identifications. Here we turn to the graphs which cannot be reduced to a line or a ring. These contributions will be collected according to the graphs of junctions which are obtained after possible identifications. Then, the expansion formulae (2), (4) and (6) reduce to the form:

$$-\frac{A'}{VkT}=-\left(\frac{A'}{VkT}\right)_{HNC}-\frac{A''}{VkT}, \tag{12}$$

$$-\frac{\mu'}{kT}=-\left(\frac{\mu'}{kT}\right)_{HNC}-\frac{\mu''}{kT}, \tag{13}$$

$$w(r)=w(r)_{HNC}+w''(r), \tag{14}$$

where $-A''/VkT$, $-\mu''/kT$ and $w''(r)$ are equal to the right-hand sides of (2), (4) and (6) respectively if we replace all the b_{ij} thereby $z(r_{ij})+z_S(r_{ij})$ and if we add a restriction about the sum by that in the graphs all the coordinates are junctions except for 1 and 2 for $w''(r_{12})$ and 1 for μ'' and there are no identifiable parts.

§ 6. Variational principle for the HNC approximation

The formulae for the free energy in the HNC approximation (11) is written by the use of (8), as

$$-\left(\frac{A'}{NkT}\right)_{HNC}=\frac{\rho}{2}\int d\boldsymbol{r}\left\{[b(r)+1]e^{z_S(r)}-1-z_S(r)\right\}$$
$$+\frac{1}{2\rho V}\sum_k\left\{-\ln(1-\rho Z(k))-\rho Z(k)-\frac{\rho^2}{2}[Z(k)+Z_S(k)]^2\right\}. \tag{15}$$

Now it is seen that the set of equations (7) and (8) which determines $z(r)$ and $z_S(r)$ is obtained by the variational principle which makes the value of the right-hand side of (15) stationary; the variation about $z(r)$ and $z_S(r)$ gives us

$$\delta\left(-\frac{A'}{NkT}\right)_{HNC}=\frac{\rho}{2}\int d\boldsymbol{r}\,\delta z_S(r)\left\{[b(r)+1]e^{z_S(r)}-1-z_S(r)-z(r)\right\}$$
$$+\frac{\rho}{2V}\sum_k\delta Z(k)\left\{\frac{\rho Z(k)^2}{1-\rho Z(k)}-Z_S(k)\right\}. \tag{16}$$

The condition of extremum is (7) and (8).

If we have some suitable approximate functional forms with several parameters for $z(r)$ and $z_S(r)$ in such a form as the integrations in (15) are easily performed, we will be able to get an approximation for the free energy in the HNC approxi-

* Cf. I, § 4; II, § 5 and II, Appendix II.

mation by introducing these in $z(r)$ and $z_S(r)$ in the right-hand side and determining the parameters in the way to make it stationary.

§ 7. Equation of state

Pressure is obtained from the knowledges of the free energy and the chemical potential:

$$\frac{p}{kT}=\frac{\rho\mu}{kT}-\frac{A}{VkT}=\rho+\frac{p'}{kT} \tag{17}$$

$$\frac{p'}{kT}=\frac{\rho\mu'}{kT}-\frac{A'}{VkT}=\left(\frac{p'}{kT}\right)_{HNC}+\frac{\rho\mu''}{kT}-\frac{A''}{VkT} \tag{17'}$$

$$\begin{aligned}\left(\frac{p'}{kT}\right)_{HNC}&=\left(\frac{\rho\mu'}{kT}\right)_{HNC}-\left(\frac{A'}{VkT}\right)_{HNC}\\&=-\frac{\rho^2}{2}Z(0)+\frac{1}{2V}\sum_k\Big\{-\ln(1-\rho Z(k))-\rho[Z(k)+Z_S(k)]\\&\quad+\frac{\rho^2}{2}[Z(k)+Z_S(k)]^2\Big\}.\end{aligned} \tag{18}$$

This formula is easily obtained also by directly differentiating the formula for the free energy (15) with respect to V with the consideration that the right-hand side of (16) is zero and so the V dependences of $z(r)$ and $z_S(r)$ need not be considered.

On the other hand, the pressure is calculated by the equation

$$p'=-\frac{\rho^2}{6}\int d\boldsymbol{r}\, g(r)\,\frac{d\phi(r)}{dr}r. \tag{19}$$

Then we can calculate the pressure by approximating $g(r)$ in this formula by $g(r)_{HNC}$ given by (5) and (9):

$$p'_{HNC}=-\frac{\rho^2}{6}\int d\boldsymbol{r}\, r\frac{d\phi(r)}{dr}e^{-\phi(r)/kT+z_S(r)}. \tag{20}$$

The direct confirmation of the identity of (18) and (20) is obtained by integrating (18) partially.*

---

* (18) with $Z(0)$ replaced by $\int d\boldsymbol{r}\, z(r)$ has the form

$$\int_0^\infty 4\pi r^2\, dr\,\sigma(r)+\frac{1}{8\pi^3}\int_0^\infty 4\pi k^2\, dk\,\tau(k).$$

This is partially integrated as

$$\frac{4\pi}{3}r^3\sigma(r)\Big|_{r=0}^{\infty}-\frac{4\pi}{3}\int_0^\infty r^3 dr\frac{d\sigma(r)}{dr}+\frac{1}{6\pi^2}k^3\tau(k)\Big|_{k=0}^{\infty}-\frac{1}{6\pi^2}\int_0^\infty k^3 dk\frac{d\tau(k)}{dk}.$$

This partial integration applied to (18) leads to (20).

Another proof of the identity of (18) and (20) is obtained by confirming that

$$\frac{\rho^2}{2} g(r)_{HNC} = \frac{\rho^2}{2}[b(r)+1]e^{z_S(r)} = \frac{\delta[A/V]_{HNC}}{\delta\phi(r)}, \tag{21}$$

which is easily proved by using (15) A' and noticing that the variations with respect to $z(r)$ and $z_S(r)$ need not be considered. Then, that (19) with $g(r)$ substituted by $g(r)_{HNC}$ is equal to $\partial A'_{HNC}/\partial V$ is the consequence of Hiroike's work.[6)]

Now, we have two formulae for the pressure, then we have two equivalent formulae also for the free energy and the chemical potential, for instance,

$$\begin{aligned}\left(-\frac{A'}{VkT}\right)_{HNC} &= \left(\frac{p'}{kT}\right)_{HNC} - \left(\frac{\rho\mu'}{kT}\right)_{HNC} \\ &= \left(\frac{p'}{kT}\right)_{HNC} + \rho^2 Z(0) + \frac{\rho}{2} z_S(0) - \frac{\rho^2}{2}\int d\boldsymbol{r}[z(r)+z_S(r)]^2;\end{aligned} \tag{22}$$

p'_{HNC}/kT is to be substituted either by (18) or by (20):

The formula for the internal energy is obtained as

$$\begin{aligned}\frac{E}{N} &= \frac{3}{2}kT + \frac{E'}{N} \\ \left(\frac{E'}{N}\right)_{HNC} &= \frac{\partial}{\partial(1/kT)}\left(\frac{A'}{NkT}\right)_{HNC} = -\int d\boldsymbol{r}\frac{\partial b(r)}{\partial(1/kT)}e^{z_S(r)} = \int d\boldsymbol{r}\phi(r)e^{-\phi(r)/kT+z_S(r)} \\ &= \int d\boldsymbol{r}\phi(r)[g(r)]_{HNC},\end{aligned} \tag{23}$$

which is the one to be obtained.

§ 8. The relation with the Born and Green integral equation

We will compare our set of equations (7) and (8) with the Born and Green integral equation for the pair distribution function.

As stated in IIIa,[3)] our set of equations reduces to

$$Z_S(k) = \frac{\rho\mathcal{E}^2 B(k)^2}{1-\rho\mathcal{E}B(k)}, \tag{24}$$

if we neglect the second and higher powers of $z_S(r)$ in (8) and approximate $z_S(r)$ by a suitable mean value

$$\mathcal{E} \equiv 1 + \overline{z_S(r)}. \tag{25}$$

This is just the linearized Born and Green integral equation.[7)]

Now, to make comparison of our set of equations with the non-linearized Born-Green integral equation, we will rewrite (7) and (8): (7) is rewritten as

$$Z_S(k) = \rho Z(k)\{Z(k)+Z_S(k)\}. \tag{26}$$

This is in the coordinate representation

$$z_S(r_{12}) = \rho \int d\boldsymbol{r}_3 z(r_{13}) \{z(r_{32}) + z_S(r_{32})\}. \tag{27}$$

Using the bipolar coordinate and introducing (8), we have

$$rz_S(r) = 2\pi\rho \int_0^\infty sds \{b(r) e^{z_S(r)} + e^{z_S(r)} - 1 - z_S(r)\}$$

$$\times \int_{-s}^{s} (r+t)\, dt \{b(|r+t|)\, e^{z_S(|r+t|)} + e^{z_S(|r+t|)} - 1\}. \tag{28}$$

By the partial integration, it is

$$rz_S(r) = \pi\rho \int_0^\infty ds \left\{ \frac{db(s)}{ds} e^{z_S(s)} + \frac{dz_S(s)}{ds} [(b(s)+1)\, e^{z_S(s)} - 1] \right\}$$

$$\times \int_{-s}^{s} (t^2 - s^2)\,(r+t)\, dt \{(b(|r+t|)+1)\, e^{z_S(|r+t|)} - 1\}. \tag{29}$$

This is the Born-Green integral equation[7] if we neglect

$$\frac{dz_S(s)}{ds}[(b(s)+1)\, e^{z_S(s)} - 1] = \frac{dz_S(s)}{ds}[z(s) + z_S(s)] = \frac{dz_S(s)}{ds}[g(s) - 1]_{HNC}$$

compared with

$$\frac{db(s)}{ds} e^{z_S(s)} = -\frac{1}{kT} \frac{d\phi(s)}{ds} [g(s)]_{HNC}.$$

At low densities, the variation of $z_S(r)$ is expected to be small compared with that of $-\phi(s)/kT$ and this neglect will be allowed. However, the situation will be different at high densities where the neglect will not be justified and the author expect that our set of equations gives a better result in this region.*

§ 9. Conclusion

It has been shown that the free energy and the chemical potential in the HNC approximation are functional of the pair distribution function in that approximation and the latter satisfies a new integral equation, in which more graphs are considered correctly than in the case of Yvon, Born and Green, hence it is expected to give better results for the pair distribution function.* Moreover, our integral equation has an analytically simpler form and seems to be suited for numerical computations.

Acknowledgement

The author wishes to express his sincere thanks to Dr. K. Hiroike for his helpful discussions.

* If we consider the expansion formula for $dg(r)/dr$, we find that more graphs are taken account of in our formula than in the Born-Green one. On this point, we are arguing that our formula is better than that of Born and Green.

References

1) T. Morita, Prog. Theor. Phys. **20** (1958), 920, to be referred to as I.
2) T. Morita, Prog. Theor. Phys. **21** (1959), 361, to be referred to as II.
3) T. Morita, Prog. Theor. Phys. **23** (1960), 175, to be referred to as IIIa.
4) J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (J. Wiley, 1940).
5) E. Meeron, J. Chem. Phys. **28** (1958), 630.
6) K. Hiroike, J. Phys. Soc. Japan **12** (1957), 864.
7) H. S. Green, *The Molecular Theory of Fluids* (North-Holland Publishing Co., 1952), Chap. III, § 6.

Errata

Theory of Classical Fluids: Hyper-Netted Chain Approximation. I and II

Tohru MORITA

Prog. Theor. Phys. **20** (1958), 920; **21** (1959), 361.

As is briefly reported in the preliminary report,[3] the author erroneously neglected in I and II some graphs which were to be included in the HNC approximation. The corrections to be made when we include these graphs are as follows:

Errata for Part I

Fig. 11 is to be replaced by

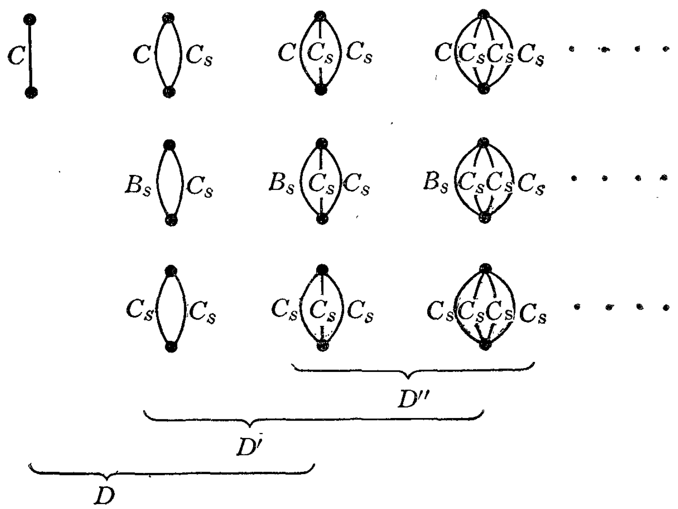


Fig. 11. D, D', D''—watermelons of C

Eq. (21), the propagation by means of D, is to be replaced by

$$f^{(2)}(\boldsymbol{r})=\{f^{(1)}(\boldsymbol{r})+h^{(0)}(\boldsymbol{r})+1\}\exp\{\Delta h^{(1)}(\boldsymbol{r})\}-1-h^{(1)}(\boldsymbol{r}).$$

Eq. (17), the contribution of D'' to $-A'/NkT$, is to be replaced by

$$\left(-\frac{A'}{NkT}\right)_{D''}=\frac{\rho}{2}\int d\boldsymbol{r}\left\{[f^{(1)}(\boldsymbol{r})+h^{(0)}(\boldsymbol{r})+1]\,[e^{\Delta h^{(1)}(\boldsymbol{r})}-1-\Delta h^{(1)}(\boldsymbol{r})]-\frac{1}{2}[\Delta h^{(1)}(\boldsymbol{r})]^2\right\}.$$

The last term of (17'), $-\frac{\rho}{4}\int d\boldsymbol{r}[\Delta h^{(1)}(\boldsymbol{r})]^2$, is to be replaced by

$$-\frac{\rho}{2}\int d\boldsymbol{r}\left\{h^{(0)}(\boldsymbol{r})\Delta h^{(1)}(\boldsymbol{r})+\frac{1}{2}[\Delta h^{(1)}(\boldsymbol{r})]^2\right\}\quad\text{or}\quad-\frac{\rho}{4}\int d\boldsymbol{r}[h^{(1)}(\boldsymbol{r})^2-h^{(0)}(\boldsymbol{r})^2].$$

The last integral of (24), $-\frac{\rho}{4}\int d\boldsymbol{r}[\Delta h^{(n-1)}(\boldsymbol{r})]^2$, is to be replaced by

$$-\frac{\rho}{4}\int d\boldsymbol{r}\left\{[h^{(n-1)}(\boldsymbol{r})]^2-[h^{(n-2)}(\boldsymbol{r})]^2\right\}.$$

The last row of Eq. (27), $-\frac{\rho}{2}\int d\boldsymbol{r} f^{(n)}(\boldsymbol{r})f^{(n-1)}(\boldsymbol{r})-\frac{\rho}{4}\int d\boldsymbol{r}\sum_{s=0}^{n-1}[\Delta h^{(s)}(\boldsymbol{r})]^2$, is to be replaced by

$$-\frac{\rho}{2}\int d\boldsymbol{r} f^{(n)}(\boldsymbol{r})h^{(n-1)}(\boldsymbol{r})-\frac{\rho}{4}\int d\boldsymbol{r}\, h^{(n-1)}(\boldsymbol{r})^2.$$

The last term of Eq. (28), $-\frac{\rho}{4}\int d\boldsymbol{r}\sum_{s=0}^{n}[\Delta h^{(s)}(\boldsymbol{r})]^2$, is to be replaced by

$$-\frac{\rho}{4}\int d\boldsymbol{r}\, h^{(n)}(\boldsymbol{r})^2.$$

The last term of Eq. (29), $-\frac{\rho}{4}\int d\boldsymbol{r}\sum_{s=0}^{\infty}[\Delta h^{(s)}(\boldsymbol{r})]^2$, is to be replaced by

$$-\frac{\rho}{4}\int d\boldsymbol{r}\, h(\boldsymbol{r})^2.$$

The second rows of formulae (30) and (30′) are to be replaced by

$$f^{(n+1)}(\boldsymbol{r})=[f^{(n)}(\boldsymbol{r})+h^{(n-1)}(\boldsymbol{r})+1]\exp\{\Delta h^{(n)}(\boldsymbol{r})\}-1-h^{(n)}(\boldsymbol{r})$$

and

$$f^{(n+1)}(r)=[f^{(n)}(r)+h^{(n-1)}(r)+1]\exp\{\Delta h^{(n)}(r)\}-1-h^{(n)}(r),$$

respectively.

The last term of Eq. (29′), $\pi\rho\int_0^\infty r^2dr\sum_{s=0}^{\infty}[\Delta h^{(s)}(r)]^2$, is to be replaced by

$$\pi\rho\int_0^\infty r^2 dr\, h(r)^2.$$

The restrictions for the products which are to be summed in Eqs. (36), (37) and the corresponding formula for $\ln g(r_{12})$ in p. 934 are to be added by that 'which have no identifiable parts'.

The second row of Eq. (48) is to be replaced by

$$f^{(n+1)}(r)=[f^{(n)}(r)+h^{(n-1)}(r)+1]\exp\{\Delta h^{(n)}(r)\}-1-h^{(n)}(r),\ n\geq 1.$$

The set of graphs which gives the d, d' and d'' in Fig. 16 is to be replaced by that which is obtained from Fig. 11 given above by replacing the large letters B and C by the small letters b and c.

Errata for Part II

In 7-8 rows from the bottom of p. 365, the sentence:

"the watermelons of C are represented by Fig. 4 if we replace the letters B and C by C and D respectively."

is to be replaced by

"the watermelons of C are represented by Fig. 5′."

and Fig. 5′ is to be drawn which is equal to Fig. 11 of Part I given just above, if we have added Greek letters ν and ν' on upper and lower vertices respectively of each graph of Fig. 11.

The last term of (17), $-\frac{1}{2}\int d\boldsymbol{r}[\Delta h^{(1)}_{\nu\nu'}(\boldsymbol{r})]^2$, is to be replaced by

$$-\int d\boldsymbol{r}\, h^{(0)}_{\nu\nu'}(\boldsymbol{r})\Delta h^{(1)}_{\nu\nu'}(\boldsymbol{r})-\frac{1}{2}\int d\boldsymbol{r}[\Delta h^{(1)}_{\nu\nu'}(r)]^2 \quad\text{or}\quad -\frac{1}{2}\int d\boldsymbol{r}[h^{(1)}_{\nu\nu'}(\boldsymbol{r})^2-h^{(0)}_{\nu\nu'}(\boldsymbol{r})^2].$$

The last term of (18), $-\frac{1}{2}\int d\boldsymbol{r}[\Delta h^{(n-1)}_{\nu\nu'}(\boldsymbol{r})]^2$, is to be replaced by

$$-\frac{1}{2}\int d\boldsymbol{r}\,[h_{\nu\nu'}^{(n-1)}(\boldsymbol{r})^2-h_{\nu\nu'}^{(n-2)}(\boldsymbol{r})^2].$$

The last term of (21), $-\frac{1}{2}\int d\boldsymbol{r}\sum_{s=0}^{n-1}[\Delta h_{\nu\nu'}^{(s)}(\boldsymbol{r})]^2$, is to be replaced by

$$-\frac{1}{2}\int d\boldsymbol{r}\,h_{\nu\nu'}^{(n-1)}(\boldsymbol{r})^2.$$

The last term of (22), $-\frac{1}{2}\int d\boldsymbol{r}\sum_{s=0}^{n}[\Delta h_{\nu\nu'}^{(s)}(\boldsymbol{r})]^2$, is to be replaced by

$$-\frac{1}{2}\int d\boldsymbol{r}\,h_{\nu\nu'}^{(n)}(\boldsymbol{r})^2.$$

The last term of (23), $-\frac{1}{2}\int d\boldsymbol{r}\sum_{s=0}^{\infty}[\Delta h_{\nu\nu'}^{(s)}(\boldsymbol{r})]^2$, is to be replaced by

$$-\frac{1}{2}\int d\boldsymbol{r}\,h_{\nu\nu'}(\boldsymbol{r})^2.$$

The second row of (24) is to be replaced by

$$f_{\nu\nu'}^{(n+1)}(\boldsymbol{r})=[f_{\nu\nu'}^{(n)}(\boldsymbol{r})+h_{\nu\nu'}^{(n-1)}(\boldsymbol{r})+1]\exp[\Delta h_{\nu\nu'}^{(n)}(\boldsymbol{r})]-1-h_{\nu\nu'}^{(n)}(\boldsymbol{r}).$$

To the restriction for the products which are to be summed in Eqs. (44), (45) and (A·10) is added 'which have no identifiable parts'.

The second row of (50) is to be replaced by

$$f_{\nu\nu'}^{(n+1)}(r)=[f_{\nu\nu'}^{(n)}(r)+h_{\nu\nu'}^{(n-1)}(r)+1]\exp[\Delta h_{\nu\nu'}^{(n)}(r)]-1-h_{\nu\nu'}^{(n)}(r),\ n\geq 1.$$