Integral Equation for Pair Distribution Function

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One of the authors has proposed the hyper-netted chain (HNC) approximation to consider by means of the Fourier transformation as many graphs as possible in the virial expansion formulas for the free energy and the pair distribution function (p.d.f.).[1] He has shown also that the p.d.f. in the HNC approximation satisfies an integral equation[2,3] which is similar to Born-Green's integral equation.[4]

In this note we shall show that the technique used in the recent derivation of the formulas in the HNC approximation[2,3] can be applied to get an exact integral equation for the p.d.f. The HNC approximation will appear as the zeroth approximation to solve this equation.

We define the function $w(r)$ which is related with the p. d. f. $g(r)$ by

$$\ln g(r) = -\frac{\phi(r)}{kT} + w(r). \qquad (1)$$

$w(r)$ can be expressed in a virial expansion form :[5]

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

where

$$b_{ij} \equiv b(r_{ij}) = e^{-\phi(r_{ij})/kT} - 1.$$

$\sum^{(W)}$ denotes that the sum is taken over all products (or graphs) in which each particle of the set $\{\boldsymbol{r}_3, \cdots, \boldsymbol{r}_{m+2}\}$ is connected to $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ by an independent path and also in which the particles $\{\boldsymbol{r}_3, \cdots, \boldsymbol{r}_{m+2}\}$ are connected among themselves independently of $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$.

We express $w(r_{12})$ symbolically by 

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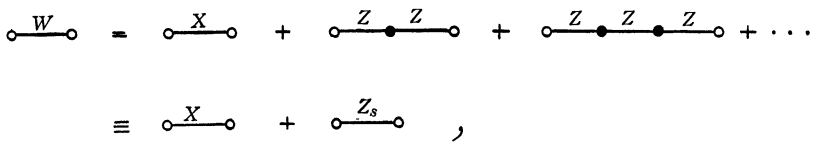
or by  .* The other symbols appearing in the following have the analogous meanings.

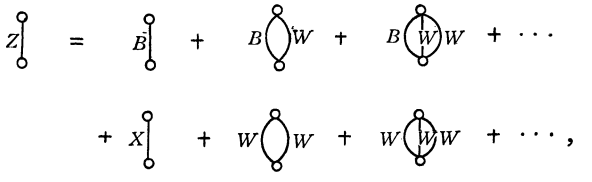
To classify the graphs appearing in $\sum^{(W)}$, we introduce the notion "s-point," which is the point by which the graph can be separated into two independent parts. We group the graphs in $\sum^{(W)}$ together by the numbers of s-points, namely



(3f)

where a black circle means an "s-point," over the coordinate corresponding to which the integration is to be performed.  and are symbols expressing $x(r_{12})$ and $z(r_{12})$ which are defined by (2) if we replace $\sum^{(W)}$ there by $\sum^{(X)}$ and $\sum^{(Z)}$, respectively, where $\sum^{(X)}$ means that the sum is taken over the graphs having no s-point among those in $\sum^{(W)}$ and $\sum^{(Z)}$ means that the sum is taken over the graphs which have no s-point and for which each particle of the set $\{\boldsymbol{r}_3, \cdots, \boldsymbol{r}_{m+2}\}$ is connected to $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ by an independent path. It is to be noted that the graphs in $\sum^{(Z)}$ need not be connected among themseleves if we remove $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$.

The graphs in $\sum^{(Z)}$ can be grouped together by the numbers of parts which is divided when we remove $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, that is



(4f)

where  denotes $b(r_{12})$. In (4f) we have taken account, in particular, of the fact that does not include and that has no s-points.

Following the analysis in the foregoing works,[1,2,3] we can express the contents of (3f) as

$$W(k)=X(k)+\frac{\rho Z(k)^2}{1-\rho Z(k)}. \qquad (3)$$

The contents of (4f) are written as

$$z(r)=b(r)e^{w(r)}+x(r)+e^{w(r)}-1-w(r),$$

which is rewritten by using (1) as

$$z(r)=g(r)-1-w(r)+x(r). \qquad (4)$$

In (3) and (4), $W(k)$, $X(k)$ and $Z(k)$ are Fourier transforms of $w(r)$, $x(r)$ and $z(r)$ respectively.

* To be more exact, it might be better to use the symbol  rather than  .

As defined above,

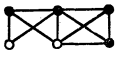
$$x(r_{12})=\sum_{m=2}^{\infty}\frac{\rho^m}{m!}\int\cdots\int d\boldsymbol{r}_3\cdots d\boldsymbol{r}_{m+2}\times\sum_{\substack{m+2\geq i>j\geq 3\\ m+2\geq k\geq 3\\ 2\geq\kappa\geq 1}}^{(X)}\Pi\, b_{ij}b_{k\kappa}. \tag{5}$$

Taking notice of the relation

$$z(r)+z_S(r)=z(r)+w(r)-x(r)=g(r)-1$$

(cf. (4) and (3f)), we can rewrite (5) as follows:

$$x(r_{12})=\sum_{m=2}^{\infty}\frac{\rho^m}{m!}\int\cdots\int d\boldsymbol{r}_3\cdots d\boldsymbol{r}_{m+2}\times\sum_{\substack{m+2\geq i>j\geq 3\\ m+2\geq k\geq 3\\ 2\geq\kappa\geq 1}}^{(X')}\Pi\,\{g(r_{ij})-1\}\{g(r_{k\kappa})-1\}. \tag{6}$$

Here $\sum^{(X')}$ means that the sum is to be taken over all those products in $\sum^{(X)}$ which consist of junctions alone (A junction means a point at which three or more lines meet.), except for $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, and for which there are no parts which are connected to any part of the graph including $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ by only two points. For example, $\sum^{(X')}$ contains  but does not contain  .

In principle a set of (1), (3), (4) and (6) can be used for determining the p.d.f. $g(r)$ exactly. In practice we must restrict the types of graphs appearing on the right-hand side of (6) within some special types. If we take $x(r)=0$ as the zeroth approximation, the set of (1), (3) and (4) is reduced to

$$W(k)=\rho Z(k)^2/\{1-\rho Z(k)\}$$

and

$$Z(r)=e^{-\phi(r)/kT+w(r)}-1-w(r),$$

which are just the equations in the HNC approximation. The next approximation will be to approximate $x(r)$ by the contribution corresponding to the graph . Such a type of integral has been treated by Nijboer and van Hove.[6] In this way we get a method to improve the HNC approximation systematically and we can in principle reach the exact p.d.f.

More detailed calculations and discussions on this subject will be published in this journal.

1) T. Morita, Prog. Theor. Phys. **20** (1958), 920.
2) T. Morita, ibid. to be published.
3) T. Morita, ibid. to be published.
4) M. Born and H. S. Green, Proc. Roy. Soc. (London) **A188** (1946), 10.
5) See for example, E. Meeron, J. Chem. Phys. **27** (1957), 1238.
6) B. R. A. Nijboer and L. van Hove, Phys. Rev. **85** (1952), 777.