grate out to r_n. In general this will not give $s(r_n)=g(r_n)=0$ as required by the boundary conditions, and from the mismatch at r_n we are able to determine an improved ϵ and p for the next trial. We repeat the procedure until our iterations for ϵ and p "settle down."

Experiment has shown[12] that the above method does not produce good eigenfunctions throughout the whole range of r. The eigenfunctions are important in our case since they are used to get the Hartree potential for the subsequent major iteration. Hence, we use the above method to get a rough idea of the correct eigenvalues and, using these as starting values, we use the following method (also suggested by Fox) to obtain the final results. We integrate both forwards and backwards and our aim is to have the forward and backward solutions meet at some central point r_c with the same height and slope. We keep the same forward boundary conditions as before and, in addition, we take as the starting conditions for our backward solution

$$s(r_n)=0, \qquad g(r_n)=0, \tag{B31a}$$

$$s(r_{n-1})=0.001, \quad g(r_{n-1})=q. \tag{B31b}$$

The backward solution must be associated with a factor k to be determined so that the normalization of the backward solution is the same as that of the forward solution. After an initial guess, the new ϵ, p, q, and k for the next trial are determined from the conditions required in order that the forward and backward solutions meet at r_c with no discontinuity. This procedure is repeated until the iterations "settle down" for ϵ in particular, and this, then, is the solution for the eigenfunction $[s(r),g(r)]$ and the single-particle energy ϵ_0. By "settle down" we mean typically in our calculations that we continue iterating until the change is less than 0.5% of the last-obtained ϵ.

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Method of Solution of the Percus-Yevick, Hypernetted-Chain, or Similar Equations

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It is shown that if the direct correlation function $c(r)$ in classical statistical mechanics vanishes beyond a range R, then the equation relating it to the radial distribution function may be used to derive a further equation which involves both functions only over the range $(0,R)$. The analytic solution of the Percus-Yevick (PY) equation for hard spheres follows as an immediate consequence, and since $c(r)$ normally tends rapidly to zero with increasing r, it is expected that the result should be of use in numerical solutions of PY, convolution-hypernetted-chain, or similar approximations.

I. INTRODUCTION

IN the classical statistical mechanics of homogeneous fluids various approximations have been proposed which involve the direct correlation function $c(\mathbf{x})$, defined by

$$h(\mathbf{x})=c(\mathbf{x})+\rho\int d\mathbf{y}\, c(\mathbf{y})h(\mathbf{x}-\mathbf{y}), \tag{1}$$

where ρ is the particle density and $h(\mathbf{x})$, the indirect correlation function, is defined in terms of the radial distribution function $g(\mathbf{x})$ by

$$h(\mathbf{x})=g(\mathbf{x})-1. \tag{2}$$

In particular, if $\phi(\mathbf{x})$ is the interaction potential and β is the Boltzmann factor $(kT)^{-1}$, the Percus-Yevick (PY) approximation[1,2] supplements (1) and (2) with the approximate relation

$$e^{-\beta\phi(\mathbf{x})}c(\mathbf{x})=\{e^{-\beta\phi(\mathbf{x})}-1\}g(\mathbf{x}), \tag{3a}$$

while the convolution-hypernetted-chain (CHNC) approximation[3,4] supplements them with

$$c(\mathbf{x})=h(\mathbf{x})-\log g(\mathbf{x})-\beta\phi(\mathbf{x}). \tag{3b}$$

In solving any such approximation it is found that the direct correlation function tends to zero with increasing $|\mathbf{x}|$ much more rapidly than the indirect correlation function[5]; for instance, the PY relation (3a) shows that $c(\mathbf{x})$ vanishes exactly outside the range of $\phi(\mathbf{x})$, while the CHNC relation (3b) predicts that it behaves as $\frac{1}{2}h^2(\mathbf{x})$ when $h(\mathbf{x})$ is small. It is therefore unfortunate that in considering the solutions of the equations the

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form of (1) demands a knowledge of both functions for all values of $\mathbf{x}$ for which $h(\mathbf{x})$ is significant, even though $c(\mathbf{x})$ may be negligible for the majority of these values.

In this paper it will be shown for three-dimensional systems with central forces that by assuming that $c(\mathbf{x})$ vanishes exactly for $|\mathbf{x}|$ greater than some range R and imposing the condition that the integral

$$\int d\mathbf{x}\, h(\mathbf{x}) \tag{4}$$

be absolutely convergent (a condition which is satisfied by any disordered fluid), a further equation can be deduced. This new equation has the property that it relates the direct and indirect correlation functions only over the range $(0,R)$, which greatly reduces the range over which it is necessary to consider $h(\mathbf{x})$ and may be expected to facilitate numerical calculations.

In many ways the present work is an extension of that of Wertheim,[6] who focussed attention on the case of the PY equation applied to a potential of finite range (this is the case where the results should be of greatest uitility). However, in addition to being of more general form, it is believed that the results represent a simplification of those of Wertheim, whose equations were complicated by the explicit consideration of a central hard core and use of $g(\mathbf{x})$ rather than $h(\mathbf{x})$.

Finally, Wertheim[7] and Thiele's[8] analytic solution of the PY equation for hard spheres is rederived by the present methods and it is shown that it is the only solution corresponding to a disordered state. As Temperley[9] has pointed out, other solutions do exist, but these must correspond to ordered states.

II. EQUATIONS FOR DISORDERED STATE

For central forces, the functions $g(\mathbf{x})$, $h(\mathbf{x})$, and $c(\mathbf{x})$ depend only on the radial distance

$$r=|\mathbf{x}|,$$

so that they may alternatively be written as $g(r)$, $h(r)$ and $c(r)$. Setting

$$H(r)=rh(r), \tag{5}$$

$$C(r)=rc(r), \tag{6}$$

and supposing that $c(r)$ vanishes when r is greater than some range R, so that

$$C(r)=0 \quad \text{when} \quad r>R, \tag{7}$$

Eq. (1) relating $h(r)$ and $c(r)$ may, in three dimensions, be written as

$$H(r)=C(r)+2\pi\rho\int_0^R ds\, C(s)\int_{|r-s|}^{r+s} dt\, H(t). \tag{8}$$

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In order to study the properties of this equation, it is convenient to replace it by the discrete approximation

$$H_i=C_i+\mu\sum_{j=1}^{n} C_j \sum_{k=|i-j|}^{i+j} \epsilon_k' H_k \tag{9}$$

for $i\geqslant 1$, where

$$\begin{aligned}
&\delta=R/(n+\tfrac{1}{2}),\\
&\mu=2\pi\rho\delta^2,\\
&H_i=H(\delta i),\\
&C_i=C(\delta i),\\
&\epsilon_k'=\tfrac{1}{2} \quad \text{if} \quad k=|i-j| \quad \text{or} \quad i+j\\
&\qquad =1 \quad \text{otherwise.}
\end{aligned}$$

[Use has been made of the fact that $H(0)$ and $C(0)$, and hence H_0 and C_0, must vanish.]

If the integer n is allowed to tend to infinity, then the solutions of (9) should tend to those of (8), provided only that $H(r)$ and $C(r)$ satisfy the physically reasonable condition of piecewise continuity. In fact (9) is simply the result a numerical analyst would obtain by applying the trapezoidal integration rule to (8). In the discrete approximation, Eq. (7) becomes

$$C_i=0 \quad \text{when} \quad i>n. \tag{10}$$

Just as Wertheim and Thiele found it convenient to introduce the Laplace transforms of the continuous functions, so it is desirable to adopt an analogous procedure with the discrete quantities and define

$$U(z)=\sum_{i=1}^{\infty} H_i z^i, \tag{11}$$

$$V(z)=\sum_{i=1}^{n} C_i z^i. \tag{12}$$

Introducing the function

$$T(z)=\frac{1}{2}\frac{1+z}{1-z}\{V(z^{-1})-V(z)\} \tag{13}$$

$$=T_0+\sum_{j=1}^{n} T_j(z^j+z^{-j}), \tag{14}$$

where, if

$$\begin{aligned}
\epsilon_{jk}&=\tfrac{1}{2} \quad \text{when} \quad j=k\\
&=1 \quad \text{otherwise},
\end{aligned}$$

the T_j are given by

$$T_j=\sum_{k=j}^{n} \epsilon_{jk} C_k, \tag{15}$$

and defining the function

$$Q(z)=Q_0+\sum_{j=1}^{n-1} Q_j(z^j+z^{-j}), \tag{16}$$

where

$$Q_j = \sum_{k=j+1}^{n} H_{k-j} T_k , \tag{17}$$

it is found that on multiplying (9) by z^i and summing over i a relation is obtained between $U(z)$, $V(z)$, $T(z)$, and $Q(z)$, namely

$$U(z) = V(z) + \mu\{U(z)T(z) - Q(z)\} . \tag{18}$$

This relation may be written in the form of an equation for $U(z)$:

$$U(z) = A(z)/B(z) , \tag{19}$$

where

$$A(z) = V(z) - \mu Q(z) , \tag{20}$$

$$B(z) = 1 - \mu T(z) . \tag{21}$$

At this stage it should be noted that $V(z)$, $T(z)$ and $Q(z)$ are determined solely by $C_1, \cdots, C_n$ and $H_1, \cdots, H_n$. Thus expanding both sides of (19) as a power series in z and equating coefficients in principle enables H_{n+1}, H_{n+2}, etc. to be determined in terms of $C_1, \cdots, C_n$ and $H_1, \cdots, H_n$. It will now be shown that the condition that the integral (4) be absolutely convergent, which in the present context implies that the sum

$$\sum_{i=1}^{\infty} i H_i \tag{22}$$

should be absolutely convergent, leads to a set of n equations relating $C_1, \cdots, C_n$ and $H_1, \cdots, H_n$ (without reference to the higher H_i coefficients).

The requirement that (22) be absolutely convergent implies that $U(z)$, which from (19) is a rational function, should have no poles inside or on the unit circle. However, $B(z)$ is a polynomial of degree n in the expression $z+z^{-1}$, so that its zeros occur in pairs of type σ, σ^{-1} and at least n of these must be inside or on the unit circle. It follows that these zeros must also be zeros of $A(z)$, and hence if $B(z)$ is written as

$$B(z) = b \prod_{i=1}^{n} (z - \sigma_i)(z - \sigma_i^{-1}) , \tag{23}$$

where $|\sigma_i| \leqslant 1$, then as $A(z)$ is of the form

$$z^{-(n-1)} \times \text{polynomial of degree } 2n-1 ,$$

it must be possible to write $A(z)$ as

$$A(z) = z^{-(n-1)} Y(z) \prod_{i=1}^{n} (z - \sigma_i) , \tag{24}$$

where $Y(z)$ is a polynomial of degree $n-1$. It follows from (23) and (24) that a function

$$S(z) = b^{-1} Y(z) Y(z^{-1}) \tag{25}$$

exists such that the function

$$\Gamma(z) = A(z)A(z^{-1}) - B(z)S(z) \tag{26}$$

vanishes identically.

Inspection of (25) and (26) shows that $S(z)$ and $\Gamma(z)$ are both polynomials in $z+z^{-1}$, of degree $n-1$ and $2n-1$, respectively, so that they may be written as

$$S(z) = S_0 + \sum_{j=1}^{n-1} S_j (z^j + z^{-j}) \tag{27}$$

and

$$\Gamma(z) = \gamma_0 + \sum_{j=1}^{2n-1} \gamma_j (z^j + z^{-j}) . \tag{28}$$

As $\Gamma(z)$ is identically zero, each of the γ_j must vanish and it is apparent that this gives $2n$ equations relating $C_1, \cdots, C_n$, $H_1, \cdots, H_n$ and $S_0, \cdots, S_{n-1}$. In the following section it will be shown that the S_i can be eliminated from the equations, leaving n relations between $C_1, \cdots, C_n$ and $H_1, \cdots, H_n$.

The reason for using the discrete approximation (9) rather than the continuous equation (8) should now be apparent, for the "Laplace transforms" become explicit polynomials, so that it is possible to count the number of poles of the transform of the indirect correlation function and hence the number of equations imposed by the condition that (4) and (22) be absolutely convergent. This avoids the analyticity problems that are encountered in working directly with (8), while it will be seen later that when the discrete equations are simplified and written explicitly the continuum limit may be regained immediately.

III. DERIVATION OF FINAL RELATION

Substitution of the explicit forms (20) and (21) of $A(z)$ and $B(z)$ into (26) leads to the result that

$$\Gamma(z) = V(z)V(z^{-1}) - S(z) - \mu\{Q(z)F(z) - T(z)S(z)\}, \tag{29}$$

where

$$F(z) = V(z) + V(z^{-1}) - \mu Q(z) . \tag{30}$$

$S_0, \cdots, S_{n-1}$ may now be determined by equating the coefficients $\gamma_n, \cdots, \gamma_{2n-1}$ of $z^n, \cdots, z^{2n-1}$ to zero, and inspection of (29) shows that the first two terms on the right-hand side are of degree $n-1$, so that only the bracketed term contributes to this procedure. Despite this simplification the evaluation of the S_i still appears to involve a complicated matrix inversion, but if the calculation is carried out in terms of the coefficients $F_0, \cdots, F_n$ of $F(z)$, i.e.,

$$F(z) = F_0 + \sum_{j=1}^{n} F_j (z^j + z^{-j}) , \tag{31}$$

and the coefficients Q_i of the $Q(z)$ which occurs explicitly in (29) are replaced by their values as given by (17),

then it is found on equating $\gamma_{2n-1}, \gamma_{2n-2}, \cdots, \gamma_n$ successively to zero that the S_i are given quite simply by

$$S_i = \sum_{k=i+1}^{n} H_{k-i} F_k . \tag{32}$$

As this appears to be a quite fortuitous chance, it is worthwhile pointing out that (32) could have been derived more directly by noting from (19) and the vanishing of $\Gamma(z)$ that

$$S(z) = U(z) A(z^{-1}) . \tag{33}$$

Since $A(z^{-1})$ is the same as $F(z)$ to order z^{-1}, the result (32) follows immediately by equating the coefficients of $z^{1-n}, \cdots, z^{-1}, 1$ in an expansion of both sides of (33).

As all the functions occurring in the definition of $\Gamma(z)$ can now be specified explicitly in terms of $C_1, \cdots, C_n$ and $H_1, \cdots, H_n$, it is possible to write $\gamma_0, \cdots, \gamma_{n-1}$ solely in terms of these quantities. Firstly, using the forms (17) and (32) of the Q_i and S_i, equating coefficients of both sides of (29) yields

$$\begin{aligned}\gamma_j = \sum_{k=j+1}^{n} \{ & C_{k-j} C_k - H_{k-j} F_k \\ & - \mu \sum_{m=1}^{n} H_m (T_k F_{|k-j-m|} - F_k T_{|k-j-m|}) \\ & + \mu \sum_{m=1}^{n+j-k} H_m (T_k F_{k-j+m} - F_k T_{k-j+m}) \}\end{aligned} \tag{34}$$

for $j = 0, \cdots, n-1$.

Fortunately one further simplification occurs in the working, for substituting the expression for F_j obtained from (30) and (31) and using the definitions (15) and (17) of the T_j and Q_j, it is found that $\gamma_0, \cdots, \gamma_{n-1}$ can all be written in the form

$$\gamma_j = \sum_{k=j+1}^{n} D_{k-j} C_k . \tag{35}$$

The calculation of $D_1, \cdots, D_n$ is tedious but quite straightforward, so that in the interests of brevity the details will not be included here. It is found that the D_i may be written as

$$\begin{aligned} D_i = C_i - H_i & + \mu \sum_{j=2}^{i} \epsilon_{ij} \sum_{k=1}^{j-1} H_k H_{j-k} \\ & + 2\mu \sum_{j=1}^{n} C_j \{ \sum_{k=1}^{i} \epsilon_{jk} H_k - \sum_{k=1}^{|i-j|} \epsilon_{|i-j|,k} H_k \} \\ & + \mu^2 \sum_{j=1}^{n} C_j \sum_{k=1}^{i} \epsilon_{ik} \{ \tfrac{1}{2} H_j H_k + W_{jk} \} , \end{aligned} \tag{36}$$

where the quantities W_{jk} are defined by an antisymmetry relation,

$$W_{jk} + W_{kj} = 0 , \tag{37a}$$

together with

$$W_{jk} = \sum_{p=1}^{j-1} H_p \sum_{q=|j-k-p|}^{j-|k-p|} \epsilon_q' H_q , \tag{37b}$$

when $j > k$, ϵ_q' being defined by

$$\begin{aligned} \epsilon_q' &= \tfrac{1}{2} \quad \text{if} \quad q = |j-k-p| \quad \text{or} \quad j-|k-p| \\ &= 1 \quad \text{otherwise.} \end{aligned}$$

The form (35) of the γ_j is particularly interesting; for, equating $\gamma_{n-1}, \gamma_{n-2}, \cdots, \gamma_0$ successively to zero, it becomes apparent that they all vanish if and only if $D_1, \cdots, D_m$ and $C_{m+1}, \cdots, C_n$ are zero, where m can be any integer from 0 to n. However, such a solution is precisely equivalent to redefining R as $(m+\frac{1}{2})\delta$ and replacing the number n of nonzero C_i in the previous working by m, i.e. to shrinking the range R beyond which $C(r)$ vanishes. If it is supposed for definiteness that R is the minimum such range, then C_n cannot be zero and $D_1, \cdots, D_n$ must all vanish. Equating the right-hand side of (36) to zero thus gives n explicit relations between $C_1, \cdots, C_n$ and $H_1, \cdots, H_n$.

It is now possible to return to the continuum limit. Allowing n to tend to infinity (keeping R constant) and equating the right-hand side of (36) to zero gives the equation

$$\begin{aligned} H(r) = C(r) & + 2\pi\rho \int_0^r ds \int_0^s dt\, H(t) H(s-t) \\ & + 4\pi\rho \int_0^R ds\, C(s) \left\{ \int_0^s dt\, H(t) - \int_0^{|r-s|} dt\, H(t) \right\} \\ & + 4\pi^2\rho^2 \int_0^R ds\, C(s) \int_0^r dt\, W(s,t) , \end{aligned} \tag{38}$$

for $0 < r < R$, where $W(s,t)$ is defined by

$$W(s,t) + W(t,s) = 0 \tag{39a}$$

and

$$W(s,t) = \int_0^s du\, H(u) \int_{|s-t-u|}^{s-|t-u|} dv\, H(v) , \tag{39b}$$

when $s > t$.

Equation (38) is the desired relation, involving $C(r)$ and $H(r)$ only over the range $(0,R)$ for which $C(r)$ is nonzero. In the following section it will be shown that the use of this equation in the PY approximation for hard spheres leads immediately to the solution of Wertheim and Thiele.

IV. PERCUS-YEVICK APPROXIMATION FOR HARD SPHERES

The PY approximation for hard spheres of diameter R states that

$$c(r) = 0 , \quad r > R , \tag{40}$$

$$g(r) = 0 , \quad r < R , \tag{41}$$

so that

$$C(r)=0, \quad r>R, \tag{42}$$

$$H(r)=-r, \quad r<R. \tag{43}$$

It is apparent that the above working may be applied immediately to this system, and that $H(r)$ is now a known function over the range of interest, namely $(0,R)$, so that (38) becomes a linear equation for $C(r)$. Substituting $-r$ for $H(r)$ leads to the result

$$C(r)=-\lambda_1 r-6\eta\lambda_2 r^2/R-\tfrac{1}{2}\eta\lambda_1 r^4/R^3, \tag{44}$$

where, following Wertheim's notation,

$$\eta=\tfrac{1}{6}\pi\rho R^3, \tag{45}$$

$$\lambda_1=1-4\pi\rho\int_0^R sd\,sC(s), \tag{46}$$

$$\lambda_2=2R^{-2}\int_0^R ds\,\{1+\tfrac{1}{3}\pi\rho s^3\}C(s). \tag{47}$$

Substituting the form (44) of $C(r)$ into (41) and (42) leads to two linear equations for λ_1 and λ_2, which may be solved to give

$$\lambda_1=(1+2\eta)^2/(1-\eta)^4, \tag{48}$$

$$\lambda_2=-(1+\tfrac{1}{2}\eta)^2/(1-\eta)^4. \tag{49}$$

This is precisely the solution of Wertheim and Thiele. In principle the present method also admits solutions corresponding to replacing R in (44)–(49) by any value R' which is less than the hard-sphere diameter R, but this can be shown to violate the conditions (41) and (43). The above solution is therefore the only one that can correspond to a disordered state, where the integral (4) is absolutely convergent, and the other solutions proposed by Temperley must correspond to ordered states, where $g(r)$ need only satisfy the weaker condition that it be bounded (and of course non-negative). In this case the function $U(z)$ defined by (11) may have poles on the unit circle and it is no longer possible to obtain equations relating $C_1, \cdots, C_n$ and $H_1, \cdots, H_n$, so that there are infinitely many solutions for $C_1, \cdots, C_n$, and hence for $C(r)$ in the range $(0,R)$.

It seems likely that the study of ordered states should not be based on Eqs. (1)–(3), but that the assumption of homogeneity should be abandoned and the one-particle distribution function allowed to be some periodic function corresponding to an ordered structure. Such an approach has been employed successfully by Jancovici[10] for the three-dimensional lattice gas of hard cubes.

V. CONCLUSIONS

Although (38) has a more complicated form than the original equation (8), the elimination of the need to consider $H(r)$ beyond the range of $C(r)$ can be extremely useful, as is particularly evident in the case of the PY approximation for hard spheres. Further, it seems likely that this property could be of value in numerical computations, for in these it is always necessary to truncate the range of the functions (and possibly to use an asymptotic form beyond the truncated range) but normally the truncated range R has to be great enough for $h(r)$ to be very small compared with unity, while if (38) is used it is sufficient for R to be large enough for $c(r)$ to be very small. For effectively short-range potentials the consequent reduction in R may well more than compensate for the greater complication of the equation. In such calculations it is probably preferable to use (38) in its derivative form, i.e.

$$H'(r)=C'(r)+2\pi\rho\int_0^r dt\,H(t)H(r-t) -4\pi\rho\left\{\int_0^r ds\,C(s)H(r-s)-\int_r^R ds\,C(s)H(s-r)\right\} +4\pi^2\rho^2\int_0^R ds\,C(s)W(s,r) \tag{50}$$

for $0<r<R$.

It should be stated that while (38) is a necessary consequence of the absolute convergence of the integral (4), it has not been proved that it is a sufficient condition. However, the virial expansions obtained from (8) and (38) are identical, so that this situation is no worse than that which existed with the original equation.

It is interesting to note that a one-dimensional fluid can also be treated by the present methods, whereas in two dimensions geometrical factors occur in Eq. (1) which seem to make the problem intractable. Although emphasis has been laid on applications to statistical mechanics, (1) is of a sufficiently general form to suggest that the technique may be of use in other mathematical fields.

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