Calculation of correlation functions of hard spheres in the generalized mean spherical approximation

B. B. Deo and A. C. Naik
Department of Physics, Utkal University, Bhubaneswar 751004, Orissa, India
(Received 3 May 1982, revised manuscript received 4 November 1982)

Wiener-Hopf factorization technique as suggested by Baxter has been used to solve the Ornstein-Zernike equation for a system of hard spheres in the framework of a generalized mean spherical model. The method reported here yields unambiguous and accurate values of the radial distribution function \( g(r) \), direct correlation function \( C(r) \), and the structure function \( S(k) \). These thermodynamic quantities have been calculated from low to fairly high densities, and, with a normalized \( g(R) \), they have been compared with the molecular-dynamics values of Alder and Hecht.

I. INTRODUCTION

The experimentally determined structure function curves for simple monatomic liquids like argon, sodium, or potassium look astonishingly similar to those calculated for an assembly of hard spheres\(^1\). So it is natural to consider a statistical system of hard spheres as a practical unperturbed first reference system for dense fluids\(^2\)–\(^4\). Based on this observation, Andersen, Chandler, and Weeks\(^5\) have suggested a simple phenomenological equation for the radial distribution function,

\[
g(r) = g_0(r) e^{-\xi(r)/k_BT},
\]

where \( \xi(r) \) is a renormalized potential and \( g_0(r) \) is the hard-sphere radial distribution function. The simple Eq. (1) has been tested for several real fluids. It is in exceedingly good agreement with all available data. Obviously enough, the small discrepancies have been attributed by the above authors to be mainly due to the nonavailability of reliable hardcore values \( g_0(r) \). One of the major aims of the present work is to suggest a novel method for obtaining accurate values for \( g_0(r) \) as well as other correlation functions for the hard-sphere system.

It has to be realized that for dense fluid the determination of the \( g_0(r) \) from its basic definition involving the partition function is extremely difficult. Therefore the study of the integral equations for \( g_0(r) \) provides a better alternative and is highly instructive. There are two such well-known equations, one by Born and Green\(^6\) (BG) and the other by Ornstein and Zernike\(^7\) (OZ), with various closures. The BG equation has the advantage that it predicts a possible phase transition for a system of hard spheres\(^8\) at \( \rho R^3 = 0.95 \), where \( R \) is the hard-sphere diameter and \( \rho \) is the particle number density. But it breaks down at high density. Therefore in this paper, we shall confine ourselves to the simpler and more elegant OZ equation, which relates the direct correlation function \( C(r) \) to the total correlation function \( h(r) \) by

\[
h(r) = C(r) + \rho \int C(r')h(|r-r'|)d^3r'.
\]

(2)

The closure is made by proposing \( C(r) \) as

\[
C(r) = g(r)(1 - e^{\xi(r)/k_BT}),
\]

called the Percus-Yevick\(^8\) (PY) equation, or

\[
C(r) = h(r) - \ln[g(r) - v(r)/k_BT],
\]

called the hypernetted-chain\(^9\) (HNC) equation. Out of the two closures the PY\(^10,11\) equation is simpler and perhaps more accurate, and using this, the OZ equation can be exactly solved for hard sphere. But the disadvantage of the PY approximation is that the equations of state obtained from virial and compressibility equations are not unique. Thus the value of correlation functions will be different. Since this will be the major point of our subsequent analysis, we further explain this point. The expression for pressure\(^6\) is

\[
\frac{\rho}{k_BT} = \frac{\rho}{k_BT} - \frac{\rho}{\pi} \int_0^\infty \frac{dv(r)}{dr} g(r)r^2 dr
\]

(5)

and leads to the virial equation\(^6\) of state for the hard spheres

\[
\frac{\rho v_1}{\rho k_BT} = (1 + \eta + \eta^2 - 3\eta^3)/(1 - \eta^3),\tag{6}
\]

whereas another expression can be deduced from the compressibility\(^6\) relation

\[
\frac{1}{k_BT} \frac{\partial p}{\partial \rho} = \left[1 + \rho \int h(r) d^3r\right]^{-1}.
\]

(7)
By integrating, the pressure $p^c$ is now given by
\[ p^c/k_B T = (1 + \eta + \eta^2)/(1 - \eta)^3 \] (8)

It is called the compressibility equation of state. For low densities $\eta \to 0$ both Eqs (6) and (8) are identical, but for $\eta \to 1$, i.e., for dense fluids, one is quite different from the other. The two expressions for pressure come from the same radial distribution function. But they differ because the latter is not exact. From Eq (5), for a hard core,
\[ p/k_B T = 1 + 4\pi g(R_+) \] (9)

($R_+$ and $R_-$ are defined as $R + 0$ and $R - 0$, respectively). The two values of $g(R_+)$ so obtained will be denoted by $g^o(R_+)$ and $g^i(R_+)$ of which $g^i(R_+)$ is found to be closer to the exact value calculated by computer experiment.

We shall show that the theory can be made consistent by postulating the appropriate discontinuity in $C(r)$ at $r = R$. That there exists a jump for $C(r)$ across $R$ has already been shown by Croxton.\(^\text{12}\) He considered the restricted class of diagrams, called a small watermelon class, and obtained an expression which shows a striking jump of $C(R)$ at $r = R$.

But that does not remove the inconsistencies altogether. So we follow a different technique, which is outlined in Secs. II and III.

The Fourier transform of the OZ equation is
\[ \tilde{h}(k) = \tilde{C}(k) + \rho \tilde{C}(k) \tilde{h}(k) \] (10)

To solve this, a function $\tilde{A}(k)$ is introduced such that
\[ \tilde{A}(k) = 1 - \rho \tilde{C}(k) = (1 + \rho \tilde{h}(k))^{-1} \] (11)

A Wiener-Hopf factorization is carried out and
\[ \tilde{d}(k) = \tilde{Q}(k) \tilde{Q}(-k) \] (12)

The function $\tilde{Q}(k)$ is regular, has zeros in the lower half plane, and can be written in the form
\[ \tilde{Q}(k) = 1 - 2\pi \rho \int_0^R dt e^{ikr} Q(r) \] (13)

$Q(r)$ is a real function and is very useful for the following discussions.

For the PY approximation $C(r)$ is strictly zero beyond the hard-core diameter $R$. In this case one calculates $g^o(R)$ to arrive at the correct value of $g(R)$, Weisman, Lebowitz, and Percus\(^\text{14-17}\) have followed a mean spherical model in which $C(r)$ is extended. We have followed the treatment which represents a generalized mean spherical model where $\tilde{Q}(r)$ is extended rather than $C(r)$. This has got certain advantage in the sense that knowledge of $Q(r)$ not only gives $C(r)$ beyond $r > R$, but the whole thermodynamics also becomes clear via the inverse compressibility equation $Q(r)$ and its Fourier transform $\tilde{Q}(k)$ have to satisfy certain boundary conditions and analytic properties, respectively. So in the simplest case it is chosen as a polynomial beyond $r > R$. It is extended until $r = R + \sigma$. Then $\sigma$ is made smaller and smaller to the extent that the calculated values of $g(r)$ become independent of $\sigma$. This extrapolates to the correct value of $g^i(R_+)$ as obtained from the compressibility equation of state. It should be noted that
\[ g(R_+) - g(R_-) = C(R_+) - C(R_-) \]

is a direct consequence of the OZ equation. The value of $C(r)$ for $r < R$ is unaffected when the range is extended beyond $R$ to $R + \sigma$.

Further, the values of the structure function $S(k)$ reported in literature refer to the Fourier transform of $h^o(r)$ which would follow from less accurate $g^o(r)$. We shall report the values of $S(k)$ obtained by Fourier transforming $g^i(r)$. We also report $C(r)$ in Sec III for several densities.

It must be emphasized at this stage that none of the values of $g^o(r)$ and $g^i(r)$ agree with the molecular-dynamics (MD) data of Alder and Hecht\(^\text{18}\). These data will be tabulated under $g^\text{MD}(r)$. It is possible to obtain this $g^\text{MD}(R)$ by choosing a different adjusted value for $Q'(R_+)$. The values of $g^\text{LO}(r)$ calculated in this phenomenological way agree quite well with the MD data. The corresponding $S(k)$ values have also been calculated. These are reported in Sec IV.

II FORMALISM

The Wiener-Hopf and Baxter\(^\text{13}\) formalism has been extensively discussed in the literature.\(^\text{1}\) So a brief outline is given here with more emphasis on our method of computation of $g_0(r)$.

With the help of Eqs. (11) and (12) it can be shown that Eq (2) can be split into
\[ rC(r) = -Q'(r) + 2\pi \rho \int_0^R dt Q(t)Q(t - r) \] (14)

for $0 < r < R$ and if $C(r) = 0$ for $r > R$, and
\[ rh(r) = -Q'(r) + 2\pi \rho \int_0^R dt (r - t)h (|r - t|) Q(t) \] (15)

for $r > 0$, where $Q'(r)$ is the derivative of $Q(r)$. Since $h(r) = -1$ for $r < R$,
\[ Q'(r) = ar + b \] for $0 < r < R$ (16)

By integrating and comparing, one gets
\[ Q(r) = a/2(r^2 - R^2) + b(r - R) \] (17)

where
Once \( Q(r) \), \( h(r) \), and \( C(r) \) are known in the range \( 0 < r < R \), the value of \( h(r) \) for \( r > R \) can be obtained through the Fourier transform of

\[
\tilde{h}(k) = \left\{ \left[ \tilde{Q}(k) \tilde{Q}(-k) \right]^{-1} - 1 \right\} / \rho
\]

But the inverse transform \( h(r) \) from \( \tilde{h}(k) \) poses some computational difficulty and is found not to converge rapidly. However, this can be computed fairly accurately by Wertheim’s zone by zone method. Alternatively, Baxter has suggested to work with the one-sided Fourier transform of \( h(r) \), that is,

\[
h_+(k) = - \int_0^R dr e^{ikr} \left[ Q'(r) + 2\pi \rho \int_0^{R-r} dt \operatorname{th}(t)Q(t+r) \right] / \tilde{Q}(k)
\]

The inverse transform of \( \tilde{h}_+(k) \) leads to \( h(r) \) relatively easily for hard core alone. However, this relation is not particularly suitable if \( C(r) \) or \( Q'(r) \) exists beyond the hard core. We find an infinity-subtraction method works very well for this problem. The high-\( k \) behavior of \( \tilde{h}(k) \), denoted by \( \tilde{h}_\infty(k) \), is subtracted. The inverse transform of

\[
\Delta \tilde{h}(k) = \tilde{h}(k) - \tilde{h}_\infty(k)
\]

is calculated rather than \( \tilde{h}(k) \) itself. For the hard core \( \tilde{h}_\infty(k) \) is taken to be

\[
\tilde{h}_\infty(k) = C_\infty \cos(kR)/k^2 - S_\infty \sin(kR)/k^3,
\]

where the coefficients are

\[
C_\infty = 2R(a + b/R)
\]

and

\[
S_\infty = 2a - 4\pi \rho R \left( a + b/R \right) / \left( a + b/R \right).
\]

The \( h_\infty(r) \) is easily calculated exactly from the integral tables

\[
h_\infty(r) = S_\infty / 2 \text{ for } r < R,
\]

\[
h_\infty(r) = (S_\infty - C_\infty) / 2r \text{ for } r \geq R.
\]

The \( h_\infty(r) \) is to be added to the Fourier transform of \( \Delta \tilde{h}(k) \). It is to be noted and we emphasize that only in this way have we been able to strictly obtain \( h(r) \) close to \(-1\) for \( r < R \), which must be satisfied in all computations.

The radial distribution function \( g_0(r) \) obtained by this inversion is \( g_0(R_+) \) at \( r = R_+ \), appropriate to the more inaccurate virial equation of state. This is the \( g(r) \) normally used in all calculations using hard-core results. The structure function \( S_\infty \) calculated using Eq. (22) would also give theoretically less-accurate values.

As suggested earlier, to get the correct value of \( g_\infty(R_+) \), one has to introduce the discontinuity in \( Q'(r) \) and \( C(r) \). We shall discuss these points in Sec. III.

**III CALCULATION OF CORRELATION FUNCTIONS IN THE GENERALIZED MEAN SPHERICAL MODEL**

Assuming that \( Q(r) \) and \( C(r) \) exist beyond the hard core until, for example, \( R + \sigma \), the Baxter equation (15) becomes

TABLE I \( Q'(R_+) \) for \( g_\eta(R) \), \( g^c(R) \), and \( g^{MD}(R) \) for different densities \( \eta \) is packing fraction

<table>
<thead>
<tr>
<th>( \eta )</th>
<th>( g_\eta(R) )</th>
<th>( g^c(R) )</th>
<th>( g^{MD}(R) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.246</td>
<td>0</td>
<td>-0.11</td>
<td>-0.10</td>
</tr>
<tr>
<td>0.370</td>
<td>0</td>
<td>-0.41</td>
<td>-0.32</td>
</tr>
<tr>
<td>0.435</td>
<td>0</td>
<td>-0.79</td>
<td>-0.55</td>
</tr>
<tr>
<td>0.462</td>
<td>0</td>
<td>-1.04</td>
<td>-0.69</td>
</tr>
</tbody>
</table>
\(Q'(r) = -rh(r) + 2\pi\rho \int_0^{R+\sigma} dt (r-t) h(|r-t|)Q(t)\)

For \(r < R\) this reduces to
\[Q'(r) = Ar + B + 2\pi\rho \int_R^{R+\sigma} dt (r-t) g(|r-t|)Q(t)\]

Here
\[A = 1 - 2\pi\rho \int_0^R Q(t)dt - 2\pi\rho \int_0^{R+\sigma} Q(t)dt\]

and
\[B = 2\pi\rho \int_0^R tQ(t)dt + 2\pi\rho \int_0^{R+\sigma} tQ(t)dt\]

One can see that the last term in Eq (29) does not vanish in the region for small \(r\), \(0 < r < \sigma\). So \(Q'(r)\)
TABLE II  Calculated values of \( g_H(r) \) compared with corresponding \( g_{MD}(r) \) values for four different densities at \( \sigma = 0.1 \) and \( R = 1 \).

<table>
<thead>
<tr>
<th>( r/R )</th>
<th>0.246</th>
<th>0.370</th>
<th>0.435</th>
<th>0.462</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta )</td>
<td>( g_{MD}(r) )</td>
<td>( g_H(r) )</td>
<td>( g_{MD}(r) )</td>
<td>( g_H(r) )</td>
</tr>
<tr>
<td>1.00</td>
<td>2.07</td>
<td>2.081</td>
<td>3.30</td>
<td>3.396</td>
</tr>
<tr>
<td>1.02</td>
<td>1.910</td>
<td>1.900</td>
<td>3.000</td>
<td>3.000</td>
</tr>
<tr>
<td>1.04</td>
<td>1.849</td>
<td>1.837</td>
<td>2.77</td>
<td>2.634</td>
</tr>
<tr>
<td>1.06</td>
<td>1.780</td>
<td>1.767</td>
<td>2.470</td>
<td>2.940</td>
</tr>
<tr>
<td>1.08</td>
<td>1.747</td>
<td>1.734</td>
<td>2.36</td>
<td>2.312</td>
</tr>
<tr>
<td>1.10</td>
<td>1.712</td>
<td>1.700</td>
<td>2.10</td>
<td>1.124</td>
</tr>
<tr>
<td>1.12</td>
<td>1.676</td>
<td>1.664</td>
<td>2.03</td>
<td>2.044</td>
</tr>
<tr>
<td>1.14</td>
<td>1.643</td>
<td>1.631</td>
<td>1.96</td>
<td>1.801</td>
</tr>
<tr>
<td>1.16</td>
<td>1.615</td>
<td>1.604</td>
<td>1.90</td>
<td>1.588</td>
</tr>
<tr>
<td>1.18</td>
<td>1.588</td>
<td>1.577</td>
<td>1.84</td>
<td>1.406</td>
</tr>
<tr>
<td>1.20</td>
<td>1.561</td>
<td>1.551</td>
<td>1.79</td>
<td>1.252</td>
</tr>
<tr>
<td>1.22</td>
<td>1.536</td>
<td>1.526</td>
<td>1.74</td>
<td>1.212</td>
</tr>
<tr>
<td>1.24</td>
<td>1.512</td>
<td>1.503</td>
<td>1.69</td>
<td>1.153</td>
</tr>
<tr>
<td>1.26</td>
<td>1.489</td>
<td>1.480</td>
<td>1.64</td>
<td>1.100</td>
</tr>
<tr>
<td>1.28</td>
<td>1.468</td>
<td>1.460</td>
<td>1.59</td>
<td>1.061</td>
</tr>
<tr>
<td>1.30</td>
<td>1.449</td>
<td>1.440</td>
<td>1.54</td>
<td>1.024</td>
</tr>
<tr>
<td>1.32</td>
<td>1.433</td>
<td>1.425</td>
<td>1.49</td>
<td>0.989</td>
</tr>
</tbody>
</table>

For \( r < R \) is not necessarily linear in \( r \). However, expanding \( g(r) \) near \( r= R \) to the lowest order in \( r \), the last term in Eq. (29) becomes

\[
2\pi \rho \int_{R-\sigma}^{R+\sigma} dt (r-t) \cdot g'(R-t+r) + \cdots \cdot Q(t)
\]

Hence Eq. (29) will reduce to

\[
Q'(r) = Ar + B + 2\pi \rho g(R) \int_{R}^{R+\sigma} Q(t) dt (r-t) + \cdots
\]

(32)

which is linear. Furthermore, if one constructs the \( Q(t) \)'s beyond \( t > R \) such that

\[
\int_{R}^{R+\sigma} dt Q(t) = 0
\]

(33)
and
\[ \int_{R}^{R+\sigma} dt \, Q(t) = 0, \]

where \( Q(r) = ar + b \) for \( r < R \) with \( a \) and \( b \) given by (18)–(20). Equation (33) forms two important constraints for \( Q(r) \) beyond \( R \).

Introducing a change of variable
\[ z = 2(r - R)/\sigma - 1 \]

and using the conditions
\[ Q_{\infty}(z) \big|_{z = -1} = Q(R^{+}) = 0 \]

we find that for \( r > R \)
\[ Q_{\infty}(z) = -Q'(1 - 6z^2 + 5z^4)/16 \]
\[ + Q'(3z - 10z^3 + 7z^5)/16, \]  

where \( Q' \) is the derivative of \( Q_{\infty} \) at \( z = -1 \), and as such, Eq. (36) satisfies all the constraints of Eq (33).

The discontinuity as estimated for both \( Q'(r) \) and \( C(r) \) is shown in Fig. 1. The \( Q'(R^+) \)'s are the bottom bold points of Fig 1(a) and the \( C(R^+) \)'s are the top bold points of Fig 1(b).

The Fourier transform \( \tilde{Q}(k) \) is of the form
\[ \tilde{Q}(k) = \tilde{Q}_{hc}(k) + \tilde{Q}_{\infty}(k), \]

where \( \tilde{Q}_{hc}(k) \) is given by Eq (13) and
\[ \tilde{Q}_{\infty}(k) = -2\pi i \int_{R}^{R+\sigma} e^{ikr} Q(r) dr \]
TABLE VI

<table>
<thead>
<tr>
<th>$r/R$</th>
<th>$\eta = 0.246$</th>
<th>$0.370$</th>
<th>$0.435$</th>
<th>$0.462$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.105</td>
<td>0.410</td>
<td>0.786</td>
<td>1.080</td>
</tr>
<tr>
<td>1.09</td>
<td>-0.007</td>
<td>-0.028</td>
<td>-0.055</td>
<td>-0.075</td>
</tr>
<tr>
<td>1.18</td>
<td>-0.034</td>
<td>-0.133</td>
<td>-0.256</td>
<td>-0.351</td>
</tr>
<tr>
<td>1.27</td>
<td>-0.023</td>
<td>-0.089</td>
<td>-0.171</td>
<td>-0.235</td>
</tr>
<tr>
<td>1.36</td>
<td>-0.001</td>
<td>-0.007</td>
<td>-0.013</td>
<td>-0.019</td>
</tr>
<tr>
<td>1.45</td>
<td>0.013</td>
<td>0.053</td>
<td>0.101</td>
<td>0.139</td>
</tr>
<tr>
<td>1.54</td>
<td>0.017</td>
<td>0.068</td>
<td>0.130</td>
<td>0.179</td>
</tr>
<tr>
<td>1.63</td>
<td>0.010</td>
<td>0.041</td>
<td>0.078</td>
<td>0.108</td>
</tr>
<tr>
<td>1.72</td>
<td>-0.001</td>
<td>-0.005</td>
<td>-0.010</td>
<td>-0.015</td>
</tr>
<tr>
<td>1.81</td>
<td>-0.009</td>
<td>-0.035</td>
<td>-0.068</td>
<td>-0.093</td>
</tr>
<tr>
<td>1.90</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Transforming the integral in Eq (38) to the $z$ space one gets

$$\tilde{Q}_\infty(k) = -2\pi \sigma e^{ik(R+\sigma/2)} \int_0^1 e^{ik\sigma z^2} Q(z) dz,$$

(39)

which is more amenable to direct computation.

As before, we make an inverse transform of

$$\Delta\tilde{h}(k) = \tilde{h}(k) - \tilde{h}_\omega(k)$$

$\tilde{h}_\omega(k)$ is again given by Eq (24) with changed coefficients.

FIG. 5 $g^{MD}(r)$ values and $g^{BQ}(r)$ values are represented by the solid and dashed line, respectively, for $\eta = 0.37$

$$C_\infty = 2R(a+b/R) - 4RQ'$$

(40)

and

$$S_\infty = 2a + [24Q' - 12(a + b/R)] \eta/(1-\eta) + 64Q'R/\sigma$$

(41)

Using Eq (39) in Eq. (37) and finally making use of Eq (22) one can evaluate $S(k)$.

MD results for hard-sphere distribution functions by Alder and Hecht are available for four different densities. We now attempt to compute the $g(r)$ at these densities with the additional extension to $Q(r)$. Take, for instance, $\eta = 0.246$. The $g^{BQ}(R+)$ calculated for this density is 2.08. The $Q^{BQ}(R+)$ to obtain this $g^{BQ}(R+)$ is -0.11 Using this $Q^{BQ}(R+)$, we calculate $Q(r)$ and $g^{BQ}(r)$.

Similarly, we furnish the $Q^{BQ}(R+)$'s for $g^{BQ}(R)$, $g^{BQ}(R)$, and $g^{MD}(R)$ for four different densities in Table I. For each density $g^{BQ}(r)$ is calculated for different $\sigma$, of which $\sigma = 0.05, 0.1$, and 0.9 are reported. At a particular density, $g^{BQ}(r)$ changes appreciably from $\sigma = 0.9$ to 0.3 but there is almost no change in $g^{BQ}(r)$ for smaller values of $\sigma$, especially for $\sigma = 0.1$ and 0.05. The values of $g^{BQ}(r)$ for various $r$ up to $r/R=1.32$ are plotted in Fig 2 for three different $\sigma$, such as $\sigma = 0.0, 0.1$, and 0.9. The $g(r)$ for $\sigma = 0.1$ relates to $g^{BQ}(r)$. There is a remarkable change in $g(r)$ for $\sigma = 0.1$ in the region $r/R = 1$ and almost no change when $r/R >> 1$. The $g^{BQ}(r)$ values for $\sigma = 0.1$ are closer to MD data. So $g^{BQ}(r)$ for $\sigma = 0.1$ are compared with the MD data at four different densities in Table II.

The structure function $S^{BQ}(k)$ is computed at four different densities and plotted in Fig 3. The values are furnished in Table III. The results do not show much changes over the $S^{BQ}(k)$ in the low-$k$ region.

Even more striking is the behavior of the direct correlation function with $\sigma$. With $Q(z)$ known, $C(r)$ can be easily obtained from Eq (14). One gets
TABLE VII  Calculated values of $g_{FQ}(r)$ compared with $g_{MD}(r)$ at four different densities for $\sigma = 0.1$ and $R = 1$.

<table>
<thead>
<tr>
<th>$r/R$</th>
<th>0.246</th>
<th>0.37</th>
<th>0.435</th>
<th>0.462</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_{MD}(r)$</td>
<td>2.07</td>
<td>3.30</td>
<td>4.36</td>
<td>4.95</td>
</tr>
<tr>
<td>$g_{FQ}(r)$</td>
<td>2.07</td>
<td>3.30</td>
<td>4.36</td>
<td>4.95</td>
</tr>
<tr>
<td>$g_{MC}(r)$</td>
<td>0.37</td>
<td>0.435</td>
<td>0.462</td>
<td>0.58</td>
</tr>
<tr>
<td>$g_{MD}(r)$</td>
<td>0.37</td>
<td>0.435</td>
<td>0.462</td>
<td>0.58</td>
</tr>
<tr>
<td>$g_{MC}(r)$</td>
<td>0.46</td>
<td>0.58</td>
<td>0.70</td>
<td>0.82</td>
</tr>
<tr>
<td>$g_{MD}(r)$</td>
<td>0.46</td>
<td>0.58</td>
<td>0.70</td>
<td>0.82</td>
</tr>
<tr>
<td>$g_{MC}(r)$</td>
<td>0.58</td>
<td>0.70</td>
<td>0.82</td>
<td>0.94</td>
</tr>
</tbody>
</table>

This direct correlation function has been calculated for four different densities with varying $\sigma$. The values of $C(r)$ are given in Tables IV–VI for $\sigma = 0.1, 0.5, 0.9$. The results are plotted in Fig. 4. The hypothesized $C(r)$ now shows a peak at...
\( \frac{r}{R} = 1 \), falling to zero after two oscillations. As \( \sigma \) is decreased, the amplitudes of the small peaks increase and ultimately shrink to the axis.

**IV. CALCULATION OF \( g^{BO}(r) \)**

It is to be noted at this stage that \( g^a(r) \) and \( g^b(r) \) agree with MD data when \( r \gg R \) but differ near \( r \approx R \). However it is possible to obtain \( g^{MD}(R) \) by choosing the exact value of \( Q'(R^+) \) as shown in the third column of Table I. This changed \( Q'(R^+) \) also improves the other \( g(r) \) values which we designate as \( g^{BQ}(r) \), and the agreement with MD data is better. The comparative results of correlation functions are reported in Table VII for all the four densities, but Fig 5 is drawn only for \( \eta = 0.37 \). The \( S(k) \) are also calculated and are found not to be very much different from \( S^Q(k) \).

The merit of the technique will be further revealed when one attempts to include attractive potentials along with the hard core. In that case, one need not use the elaborate procedure of Smith, Tosi, and Hoye and Blum. One has to assume the existence of \( Q(r) \) beyond the hard core and with proper discontinuity of \( Q'(r) \) fit \( g(r) \) to the MD data for the said potential. Once \( Q(r) \) is known for the entire range, the thermodynamics becomes transparent. The work along these lines is being pursued.

**ACKNOWLEDGMENTS**

One of the authors (A C N.) gratefully acknowledges the University Grants Commission, India, for the award of a fellowship. The computational help of the Computer Centre, Utkal University, is acknowledged.

---

7[7] L Ornstein and F Zernike, Z Phys. 27, 761 (1926)
Solution of Ornstein-Zernike equation for one-dimensional fluids

B B DEO, B P DAS and A C NAIRK
Department of Physics, Utkal University, Bhubaneswar 751 004, India

MS received 19 September 1981

Abstract. The application of Wiener-Hopf factorisation procedure as adopted by Baxter has been used to solve the one-dimensional Ornstein and Zernike (OZ) equation for a fluid of interacting hard rods. Exact solution is obtained for the Kac potential in the van der Waals limit. We also obtain perturbative results which agree exactly with the lowest order calculations of Kac, Uhlenbeck and Hemmer.

Keywords: Ornstein-Zernike equation, one-dimensional fluid, hard rod, Baxter method, direct correlation function, total correlation function, radial distribution function, exponential tail, van der Waals limit, phase transition

1. Introduction

The study of statistical mechanics of fluids in one dimension has been a subject of considerable interest. A soluble one-dimensional exponentially interacting gas model was first proposed by Kac (1959). Soon afterwards rigorous solutions of the model were obtained by Kac et al. (1963). They gave an exact derivation of the partition function in the thermodynamic limit and found that for a finite range of the attractive force, the system does not show a phase transition in conformity with the results of Gursey (1950) and van Hove (1950). However, for a weak but very long range attractive force a phase transition appears which is described by the van der Waals equation. They also deduced the distribution functions, specially the pair distribution function for the interacting gas. Percus (1976) has also studied the equilibrium state of a classical fluid of hard rods in an external field. All direct correlation functions are shown to be of finite range in all pairs of variables.

Unlike the Kac model, the many body problems which are of physical interest are difficult to solve exactly. One integral equation due to Ornstein and Zernike (1926) which can be deduced by summing up majorised graphs of cluster expansion methods (Rice and Gray 1965), appears to describe the physical situations in a simpler prospective. Even this approximate integral equation requires further approximations for the direct correlation function, the convolution hypernetted chain (CHNC) and the Percus-Yevick (PY) approximations. Recently Baxter (1968) has suggested a very powerful method of solving OZ equation in PY approximation using the Wiener-Hopf technique (Morse and Feshback 1953). This has been applied successfully to study the problems in three dimensions.

It is not at all clear whether this method, when applied to the one-dimensional Kac model will reproduce the results of Kac et al. (1963) in the van der Waals limit. Since the phenomenon of phase transition in one dimension is a highly controversial
subject, it is worth-while to deduce it by other independent methods. Furthermore, the highly successful exponential approximation of Andersen and Chandler (1972) seems to disagree with the machine calculation of structure function for small wave numbers (Stell and Weis 1980). There is a need to have diverse methods of solution which can follow the manner of obtaining solution from one-dimensional models. The present note is an attempt in these directions.

We find that the Kac problem can be solved elegantly by the Baxter (1968) method. §2 describes Baxter's technique and its application to solve the problem of hard rods. A general method of solution for the interacting rods which can be extended to three dimensions is given in §3. Kac model is also solved in this section to the lowest order of perturbation in both the long and the short range limits.

2. Solution by the Wiener-Hopf and Baxter technique

2.1 General formulation

In one dimension, the oz equation is

\[ h(x) = C(x) + \frac{1}{l} \int_{-\infty}^{+\infty} dx' C(x') h(x - x'), \quad (1) \]

where \( 1/l = N/L \) is the density of hard rods and its Fourier transformed equation

\[ \tilde{h}(k) = \tilde{C}(k) + \frac{1}{l} \tilde{h}(k) \tilde{C}(k), \quad (2) \]

can be rewritten in the form

\[ (1 + \tilde{h}(k)/l) (1 - \tilde{C}(k)/l) = 1 \quad (3) \]

We define a new function \( \tilde{A}(k) \) by the relation

\[ \tilde{A}(k) = 1 - 1/l \tilde{C}(k) = (1 + 1/l \tilde{h}(k))^{-1} \quad (4) \]

For a disordered fluid, \( \tilde{h}(k) \) is finite. Consequently \( \tilde{A}(k) \) has no zeroes for real values of \( k \) and it can always be factorized (Baxter 1968) as

\[ \tilde{A}(k) \equiv \tilde{\Gamma}_1(k) \tilde{\Gamma}_2(k) \quad (5) \]

\( \tilde{\Gamma}_1(k) \) is analytic in the upper half of the complex \( k \) plane and has zeroes only in the lower half of the plane, whereas \( 1/\tilde{\Gamma}_2(k) \) is analytic in the lower half of the plane and has zeroes only in the upper half of the plane. From the defining equations and assumed analyticity it follows that (Baxter 1968)

\[ \tilde{\Gamma}_1,\tilde{\Gamma}_2(k) \sim 1 + O\left(\frac{1}{|\text{Re}\; k|}\right) \quad (6) \]
The functions \(1 - \tilde{\Gamma}_{1,2}(k)\) are therefore Fourier integrable along the real axis and the two functions defined by

\[
\Gamma_{1,2}(x) = \int_{-\infty}^{\infty} dk/2\pi \left(1 - \tilde{\Gamma}_{1,2}(k)\right) \exp(-ikx),
\]

are such that \(\Gamma_{1}(x)\) vanishes for \(x < 0\) and \(\Gamma_{2}(x)\) vanishes for \(x > 0\). Equation (4) with the help of (5) can be written in the form

\[
\frac{1}{l} C(k) = 1 - \tilde{\Gamma}_{1}(k) + 1 - \tilde{\Gamma}_{2}(k) - (1 - \tilde{\Gamma}_{1}(k))(1 - \tilde{\Gamma}_{2}(k)).
\]

From (8), one easily gets \(C(x)\) in terms of \(\Gamma_{1,2}(x)\) as

\[
C(x) = \Gamma_{1}(x) + \Gamma_{2}(x) - \frac{1}{l} \int \Gamma_{1}(t) \Gamma_{2}(x-t) \, dt.
\]

Multiplying \(\exp(-ikx)\) to both sides of the equation

\[
\tilde{\Gamma}_{1}(k) \left[1 + \frac{1}{l} \tilde{h}(k)\right] = 1/\tilde{\Gamma}_{2}(k),
\]

and integrating with respect to \(k\) from \(-\infty\) to \(\infty\) and noting that

\[
\frac{1}{l} \int_{-\infty}^{\infty} 1/\tilde{\Gamma}_{2}(k) \exp(-ikx) \, dk = 0 \text{ for } x > 0,
\]

we get

\[
h(x) = \Gamma_{1}(x) + \frac{1}{l} \int_{0}^{\infty} dt \Gamma_{1}(t) h(x-t),
\]

for \(x > 0\). Thus besides the direct correlation function \(C(x)\) and the total correlation function \(h(x)\), (9) and (11) show that a third analytic function \(\tilde{\Gamma}_{1}(x)\) can be introduced which is related to \(C(x)\) and \(h(x)\) in a convenient manner.

### 2.2 Hard rods

Following Baxter's notation let us replace \(\Gamma\) by \(Q\) in the hard rod problem. For a rod of length \(\delta\)

\[
h(x) = -1 \quad \text{for } 0 < |x| < \delta,
\]

and

\[
C(x) = 0 \quad \text{for } |x| > \delta
\]

It follows that, for \(x > \delta\)

\[
Q(x) = \Gamma_{1}(x) = 0
\]
Substituting these values in (11), we get, for $0 < x < \delta$

$$-1 = Q(x) + \frac{1}{l} \int_0^\delta Q(t) h(x-t) \, dt,$$

(13)

when both $x$ and $t$ are in the range $0$ to $\delta$, then $h(x-t) = -1$ in (13). So $Q(x)$ can be easily found and then from (9), $C(x)$ can be obtained

$$Q(x) = -l(l - \delta),$$

(14)

and

$$C(x) = -l(l - x)(l - \delta)^2,$$

(15)

which is the correct result (Wertheim 1964) Equation (11) for $x > \delta$ for non-interacting hard rods become

$$g(x) = 1 - \frac{1}{l} \int_0^\delta Q(t) \, dt + \frac{1}{l} \int_0^\delta Q(t) g(x-t) \, dt$$

(16)

The Laplace transform of $g(x)$ is obtained as

$$G(s) = \int_0^\infty \exp(-sx) g(x) \, dx = \frac{1}{[1 + s(l - \delta)] \exp(s \delta) - 1}$$

(17)

The inverse Laplace transform is easily calculated to find the radial distribution function

$$g(x) = \sum_{n=1}^\infty \theta(x - n \delta) \exp[-(x - n \delta)/(l - \delta)] \frac{(x - n \delta)^{n-1}}{(l - \delta)^n (n - 1)!}$$

(18)

where $\theta(x-n \delta)$ is the Heaviside step function, agreeing with the results of Kac et al (1963) and Zemike and Prins (1927). Thus we are assured that the one-dimensional version of Baxter's formalism together with the PY approximation solves the problem of hard rod exactly.

3 General method of solution

3.1 Interacting hard rods

To discuss the problem of interacting hard rods (Smith 1979) it is convenient to consider $C(x)$ on $x > \delta$ separately from its behaviour on $0 < x < \delta$

$$C(x) = C_0(x) \theta(\delta - |x|) + C_1(x) \theta(|x| - \delta).$$

(19)

It is important to note that $C_0(x)$ is not identical with the hard core value, even though the latter may be a good approximation to it in most of the problems of
The Fourier transform of $C(x)$, $\tilde{C}(k)$ may also be written in the form

$$\tilde{C}(k) = \tilde{C}_0(k) + \tilde{C}_s(k)$$

(20)

$C_s(k)$ can be taken as the Fourier transform of $C_1(x)$ which contains the unknown function $g(x)$ Thus one has to resort to further approximation depending upon the physical problem under consideration They proposed to approximate $C_1(x)$ by

$$C_1(x) \approx g(x) [1 - \exp(\beta v(x))]$$

(21)

where $\beta = 1/kT$ Similarly for the two regions we decompose $\Gamma(x)$ as

$$\Gamma_1(x) = \Gamma_0(x) \theta (\delta - x) + \Gamma_\infty(x) \theta (x - \delta)$$

(22)

Now we assert that

$$\Gamma_\infty(x) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \frac{\tilde{C}_s(k)}{\Gamma_s(k)} \exp(-i k x).$$

(23)

To demonstrate the correctness of this assertion, use (9) for $x > \delta$ to get

$$C_1(x) = \Gamma_\infty(x) - \frac{1}{i} \int_{x}^{\infty} \Gamma_\infty(t) \Gamma(t - x) \, dt.$$  

(24)

and then substitute (23) for $\Gamma_\infty(x)$. Then

$$C_1(x) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \exp(-i k x) \frac{\tilde{C}_s(k)}{\Gamma_s(k)} \left[ 1 - \frac{1}{i} \int_{0}^{\infty} \Gamma(t) \exp(-i k t) \, dt \right]$$

(25)

Since by definition,

$$\tilde{\Gamma}_s(k) = 1 - \frac{1}{i} \int_{0}^{\infty} \Gamma(t) \exp(-i k t) \, dt,$$

(26)

(25) follows

Once $\Gamma_\infty(x)$ is known, (11) can be used within the range $0 < x < \delta$ to get

$$\Gamma_0(x) = -\tilde{\Gamma}(0) - \frac{1}{i} \int_{\delta}^{\infty} \Gamma_\infty(t) g(x - t) \, dt,$$

(27)
where $\Gamma(0)$ is given by

$$
\Gamma(0) = \frac{1}{l-\delta} - \frac{1}{l-\delta} \int_{\delta}^{\infty} \Gamma_{\infty}(t) \, dt + \frac{1}{l(l-\delta)} \int_{\delta}^{\infty} dt \int_{\delta}^{\infty} dx \, \Gamma_{\infty}(t) \, g(x-t). \quad (28)
$$

Thus $\Gamma(x) = \Gamma_{\delta}(x) + \Gamma_{\infty}(x)$, is known. Using this $\Gamma(x)$ in (9) and (11), the functions $C(x)$ and $g(x)$ can be found out. This is illustrated below.

3.2 Kac model

As an example consider the Kac model (Kac 1959) of hard rods interacting via an exponential attraction. The weak long-ranged potential is

$$
v_\delta(x) = -a \exp (-\gamma |x|) \theta(|x| - \delta) \quad (29)
$$

In the limit $\gamma \to 0$, the range of the potential tends to infinity and as $a \to 0$, the potential becomes only weakly attractive. The limit where both the $a$ and $\gamma$ tend to zero but with $a/\gamma = a_0$ finite, is called the van der Waals limit. This limiting procedure actually provides the escape from the Gursey-Van Hove results.

From (21), for $\beta = \nu$ tending to zero,

$$
C_\delta(x) \approx \nu \exp (-\gamma |x|) g(x) + O(\nu^3) + \ldots. \quad (30)
$$

Omitting $\nu^3$ and the higher order terms, the Fourier transform of (30) is

$$
\tilde{C}_\delta(k) = \nu \left[ G(\gamma - ik) + G(\gamma + ik) \right], \quad (31)
$$

where

$$
G(\gamma \mp ik) = \int_0^\infty dx \, g(x) \exp \left[ -x(\gamma \mp ik) \right]. \quad (32)
$$

Substituting (31) in (23) and integrating we get

$$
\Gamma_{\infty}(x) = \frac{\nu \exp (-\gamma x)}{\tilde{\Gamma}_\delta(-i\gamma)}. \quad (33)
$$

Using (33) in (27), we get

$$
\Gamma_{\delta}(x) = -\tilde{\Gamma}(0) - \frac{\nu}{l} G(\gamma) \exp (-\gamma x) \frac{1}{\tilde{\Gamma}_\delta(-i\gamma)}, \quad (34)
$$

where

$$
G(\gamma) = \int_0^\infty \exp (-\gamma t) \, g(t) \, dt. \quad (35)
$$
The Fourier transform of $\Gamma(x)$ is
\[
\tilde{\Gamma}(k) = 1 + \frac{1}{l} \tilde{\Gamma}(0) \frac{\exp(ik\delta) - 1}{ik} + \frac{\nu G(\gamma)}{l^2} \frac{1 - \exp[-\delta(\gamma - ik)]}{\tilde{\Gamma}_d(-\gamma)(\gamma - ik)} - \frac{\nu \exp[-\delta(\gamma - ik)]}{l \tilde{\Gamma}_d(-\gamma)(\gamma - ik)}.
\]

(36)

Approximating $G(\gamma)$ by its hard core value $1/\gamma$ (in the limit $\gamma \to 0$), defining $-\nu_0 = \nu/\gamma$ and putting $k = 0$,
\[
\tilde{\Gamma}(0) \approx \frac{l}{l - \delta} - \frac{\nu_0}{l \tilde{\Gamma}_d(-\gamma)}.
\]

(37)

For $k = \nu \gamma$, using (37) and (26), (36) becomes
\[
\tilde{\Gamma}(\nu \gamma) \approx \frac{l}{l - \delta} - \frac{\nu_0}{2l \tilde{\Gamma}(\nu \gamma)}.
\]

(38)

Solving for (38)
\[
\tilde{\Gamma}(\nu \gamma) = \frac{1}{2} \left[ \frac{l}{l - \delta} \pm \left\{ \left( \frac{l}{l - \delta} \right)^2 - 2\nu_0 l \right\}^{1/2} \right]
\]

(39)

Substituting (38) and (39) in (37)
\[
\tilde{\Gamma}(0) = \left[ (l/l - \delta)^2 - 2\nu_0 l \right]^{1/2}
\]

(40)

It is to be noted that (40) can be very simply obtained if one assumes $\tilde{C}_d(k)$ to be given by the hard core value. Then
\[
\tilde{\Gamma}(0)^2 = 1 - \frac{1}{l} [\tilde{C}_d(0) + \tilde{C}_d(0)]
\]

\[
= \left( \frac{l}{l - \delta} \right)^2 - \frac{2\nu_0}{l}.
\]

The inverse compressibility equation of state (Baxter 1968) is
\[
\beta \left. \frac{\partial p}{\partial \beta} \right|_{T} = \tilde{\Gamma}(0)^2 = (l/l - \delta)^2 - 2\nu_0 l,
\]

(41)

and leads as usual to the van der Waals equation of state.
\[
p = \frac{\beta}{\beta(l - \delta)} - \alpha_0 l^2,
\]

(42)
where \( \alpha_0 = a/\gamma \) Thus in the van der Waals limit there is phase transition in the Baxter method of solution in one dimension.

It is not obvious, whether the highly involved expressions for the radial distribution function obtained by Kac et al (1963) can also be obtained by this simple and elegant method. To examine this point, let us denote the hard core values as

\[
1 - \frac{1}{l} \tilde{C}_0 (k) = \frac{\tilde{Q} (k) \tilde{Q} (-k)}{\gamma^2 + k^2}
\]

So,

\[
\tilde{\Gamma}_1 (k) \tilde{\Gamma}_2 (k) = 1 - \frac{1}{l} \left[ \tilde{C}_0 (k) + \tilde{C}_s (k) \right]
\]

\[
= \frac{\tilde{Q} (k) \tilde{Q} (-k)}{\gamma^2 + k^2} \left[ \gamma^2 + \beta^2 \right],
\]

where,

\[
B^2 (k) = 1 - \nu \left[ \frac{\partial}{\partial y} \left. \frac{G(\gamma - ik) + G(\gamma + ik)}{\tilde{Q}(k) \tilde{Q}(-k)} \right|_{y=0} \right] [\gamma^2 + k^2].
\]

The crucial and novel point in this analysis is to be able to correctly guess the values of \( \tilde{\Gamma}_1 (k) \) and \( \tilde{\Gamma}_2 (k) \) so that these latter functions satisfy the required analytic properties. After some intuitive thought and following the discussion by Morse and Feshback (1953) we found that they are as follows

\[
\tilde{\Gamma}_1 (k) = \frac{k^2 + \gamma^2 \beta^2 (k)}{(k + ry) C} \tilde{Q} (k),
\]

and

\[
\tilde{\Gamma}_2 (k) = \frac{C}{k - ry} \tilde{Q} (-k),
\]

where \( C \) is an unknown constant factor 1/\( \tilde{\Gamma}_2 (k) \) cannot have zeroes on the lower half of the complex \( k \) plane. So it has zeroes at \( k = +i \gamma \). The conjugate pole occurs in \( \tilde{\Gamma}_1 (k) \).

We emphasize here, that the approach of other authors in this regard can be entirely erroneous specially in the case of three dimensions (Hoye and Blum 1977, Blum and Hoye 1978). In perturbative analysis, much notice is not taken of the analyticity requirements of the exact solution which can be quite different from the unperturbed case.

From equations (4), (5) and (44) we have,

\[
\tilde{Q} (k) \left[ 1 + \frac{1}{l} \tilde{h} (k) \right] = \frac{k^2 + \gamma^2}{k^2 + \gamma^2 \beta^2 (k)} \frac{1}{\tilde{Q} (-k)}
\]

On rearranging the above equation, multiplying both the sides with \( \exp (-ikx) \) and integrating with respect to \( k \) from \( -\infty \) to \( \infty \) we get

\[
h (x) = Q (x) + \frac{1}{l} \int_0^\infty dt \quad Q (t) \quad h (x - t) + \nu \int_{-\infty}^\infty \frac{dk \exp (-ikx)}{2\pi} \quad \tilde{Q} (-k)
\]

\[
\times \frac{k^2 + \gamma^2}{k^2 + \gamma^2 \beta^2 (k)} \left[ \frac{G(\gamma - ik) + G(\gamma + ik)}{\tilde{Q}(k) \tilde{Q}(-k)} \right]
\]

\[
(48)
\]
The Laplace transform is

\[ G(s) = G_0(s) + \frac{v}{B(0)} \frac{(l-\delta)^4 s^2 \exp(2s\delta)}{l^2} \frac{(s+\gamma) G(s + \gamma)}{\lambda^2(s)(s + \gamma B)} \tag{49} \]

where \( \lambda(s) = [1 + s(l - \delta)] \exp(s\delta) - 1 \) and

\[ G_0(s) = \frac{l}{\lambda(s)}, \tag{50} \]

is the hard core value. Equation (49) can be written as

\[ G'(s) = G_0(s) + \Delta G(s), \tag{51} \]

where

\[ \Delta G(s) = v \frac{(l-\delta)^4 s^2 \exp(2s\delta)}{B(0) l^2} \frac{s + \gamma}{\lambda^2(s)(s + \gamma B)} G(s + \gamma). \tag{52} \]

Incorporating van der Waals limit the first order perturbation effect for short ranges is

\[ \Delta G(s) = v \frac{(l-\delta)^4 s^2 \exp(2s\delta)}{B(0) l} \frac{s + \gamma}{\lambda^2(s)}. \tag{53} \]

In the long range, \( S \) is replaced by \( Sy \) and then the limit \( \gamma \to 0 \) is taken with the result

\[ \Delta G(s) = v_0 (l-\delta)^4/[B(0) l^4 (s + B)]. \tag{54} \]

The equations (53) and (54) agree exactly with the results of Kac et al (1963) and Lebowitz and Percus (1963) both in the long range and the short range limits.

4. Conclusion

The application of Wiener-Hopf method of factorisation has greatly facilitated the study of oz equation in PY approximation. In a one-dimensional system there is a phase transition in van der Waals limit and for weakly attracting hard rods the results are in total agreement with the results of Kac et al (1963) at least to the first order of perturbation. Baxter’s method can be used with confidence in perturbative study of the statistical mechanics of fluids in three dimensions as well.

Acknowledgement

The authors BFD and ACN are grateful to the UGC, India for the award of teacher fellowships.
References

Andersen H C and Chandler D 1972 J Chem Phys 57 1918
Baxter R J 1968 Aust J Phys 21 563
Gursey F 1950 Proc Cambridge Philos Soc 46 182
Kac M 1959 Phys Fluids 2 8
Kac M, Uhlenbeck G E and Hemmer P C 1963 J Math Phys 4 216, 229
Ornstein L S and Zernike F 1926 Phys Z 27 761
Rice S A and Grey P 1965 The statistical mechanics of simple liquids (New York: John Wiley)
Smith E 1979 Mol Phys 38 823
Van Hove L 1950 Physica 16 137
Wertheim M S 1964 J Math Phys 5 643
Zernike F and Prins J A 1927 Z Phys 41 184