Numerical and analytical studies of the long-ranged solutions of the Yvon–Born–Green equation

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In this paper we give a detailed description of our numerical studies of the critical behavior of the Yvon–Born–Green (YBG) equation in various dimensions and the conclusions which we believe these studies warrant. A central issue in these studies is the relationship between the convergence of the numerical methods used to solve the YBG equation, the long-ranged nature of the solutions, and possible bifurcations in the solution structure of the equation. An understanding of these relationships is essential to the construction of reliable numerical solutions in the critical region of the YBG equation and is likely to be equally important for a large class of nonlinear integral equations with short-ranged kernels. We give some analytic models and numerical techniques which are effective in exploring these questions. From these studies the following conclusions concerning the critical behavior of the YBG equation are drawn: (1) For d = 3 there is a region of density and temperature in which the correlations are long ranged but this range never becomes more than 13 hard-core radii. The compressibility remains finite, though large, in this region. There is no true critical point for d = 3 but rather a region of "near critical" behavior. (2) For d = 5, 6 there is a (stability) line in the density-temperature plane and, as that line is approached, the range of numerical solutions and the compressibility appear to increase without bound. Inside this stability line solutions cannot be found by the usual numerical techniques. All of the data near the stability line can be fit, quite accurately, with mean-field theory exponents. The thermodynamic behavior of the correlation range and the isothermal compressibility have the scaling (homogeneity) properties of a mean-field or van der Waals-type theory.

INTRODUCTION

Recently, there have been several analytic and numerical studies3–5 of the Yvon–Born–Green (YBG) equation for the pair distribution function. The YBG equation is generated by truncating the BBGKY hierarchy using the Kirkwood superposition approximation. These studies have concentrated on the region of density and temperature for which the solutions of the YBG equation have ranges large compared to that of the intermolecular potential. This is in the region in which the compressibility, determined as a spatial integral of the pair correlation function, becomes large and where one would expect to find the thermodynamic critical behavior of the YBG equation. Earlier numerical studies6 appeared to give very realistic values for some of the critical exponents for the spatial dimension d = 3 for a system of molecules interacting via a hard-core attractive square well intermolecular potential; these studies suggested that the YBG equation might, in some sense, give a correct description of the critical behavior of real fluids. The more recent studies1–2 were undertaken to see to what extent this might be so and to study the effect of the spatial dimension d on the critical behavior of the YBG equation. These studies have given, we believe, a fairly complete and coherent picture of the critical behavior of the YBG equation which is different from that suggested by the earlier studies. This picture, and the evidence for it, has emerged through several papers,1–5 some of which are letters of restricted length and in which methods and results could only be summarized. A coherent and extensive account of the primarily analytic studies of the YBG equation is available3 and it is the purpose of this paper to provide a similar account of the primarily numerical studies. There are, of course, points of intimate connection between the two approaches which we shall discuss in some detail.

In Sec. II we summarize the results of the analytic studies of the YBG equation with particular emphasis on questions raised by these studies which can, at present, only be answered through the construction of numerical solutions. In Sec. III we describe in some detail the numerical method used in constructing the solutions and describe the convergence difficulties of these iterative procedures in the critical region. These convergence problems, which are the numerical analog of the critical slowing down of the approach to equilibrium seen in experiments on real systems, present the same kind of problems that arise experimentally in the determination of critical behavior. In particular, as a critical point is approached the rate of convergence of the iterative process becomes very slow so that, as a practical matter, one cannot construct solutions arbitrarily close to the critical point and one must assume or plausibly argue that certain behaviors can be extrapolated to the critical point. It is particularly tricky to distinguish numerically between the case where a true critical point exists (which we believe is true for d = 5, 6) and the case where there is a region of very long-ranged solutions which never quite become critical (which we believe is true for d = 3).

Because of the central role of these convergence
II. SUMMARY OF ANALYTIC RESULTS

The YBG equation for the pair correlation function \( g(r) \) can be written, for spherically symmetric potentials, as:

\[
-\frac{\partial \ln g(r)}{\partial r} = \frac{1}{k_B T} \frac{\partial \phi(r)}{\partial r} + \frac{\rho}{k_B T} \int r \cdot \frac{D\phi(s)}{Ds} g(s) [g(|r-s|) - 1] \, ds,
\]

(2.1)

where \( \phi(r) \) is the intermolecular potential, \( \rho \) is the number density, \( k_B \) is Boltzmann’s constant, \( T \) is the temperature, and \( r \) and \( s \) are \( d \)-dimensional spatial coordinates. If the \( s \) integral is converted to polar coordinates with \( r \) along the polar axis then \( d = 2 \) angular integrals can be performed on Eq. (2.1) to yield

\[
-\frac{\partial \ln g(r)}{\partial r} = \frac{\partial \phi(r)}{\partial r} + \frac{\rho \Omega_{d-1}}{k_B T} \int_0^r \frac{1}{s} \frac{D\phi(s)}{Ds} g(s) [g(|r-s|) - 1] \, ds,
\]

(2.2)

where

\[
\Omega_{d-1} = \frac{(d-1) \pi^{(d-1)/2}}{\Gamma\left(\frac{d}{2} + \frac{1}{2}\right)}
\]

is the area of the unit sphere in \( (d-1) \) dimensions, \( \phi \) is the angle between \( r \) and \( s \), and \( |r-s| = (r^2 + s^2 - 2rs \cos \phi)^{1/2} \).

Equation (2.2) is the nonlinear integrodifferential equation which should be solved with the boundary condition

\[
g(r) - 1 \text{ as } r \to \infty
\]

(2.3)

to find \( g(r) \) as a function of \( r \), \( \rho \), and \( T \) for any given potential \( \phi(r) \) and dimension \( d \). The full YBG Eq. (2.2) is sufficiently complex that it has not been solved for arbitrary \( \rho \) and \( T \) by analytic techniques and the behavior of its solutions as \( \rho \) and \( T \) are varied must, at present, be investigated by numerical methods such as those described in the next section.

If however, there is a region of \( \rho \) and \( T \) for which the solutions of Eq. (2.2) are long ranged and slowly varying with respect to \( r \), then Eq. (2.2) can be well approximated \(^{1,2,5}\) by a much simpler nonlinear differential equation which gives useful information about the \( r \) dependence, but not the \( \rho \) or \( T \) dependence, of the solutions of the YBG equation. More specifically if one assumes that the spatial derivations of \( g \) behave, for \( r \approx R_1 \) (where \( R_1 \) is somewhat greater than \( R_0 \), the range of the potential), as

\[
\frac{g^{(1)}(r)}{R^{(1)}(r)} = \frac{1}{\xi} + O\left(\frac{1}{r}\right)
\]

(2.4)

where

\[
g^{(1)}(r) = \frac{Dg(r)}{Dr}
\]

and \( \xi \) is a correlation length with \( \xi \gg R_0 \), then one can systematically approximate Eq. (2.2) for \( r \approx R_1 \) by an expansion in the two small parameters \( R_0/r \) and \( R_0/\xi \) with no restrictions on the relative size of \( r \) and \( \xi \). A convenient, but less important assumption, is that \( g(r) - 1 = h(r) \)

is small compared to unity for \( r > R_1 \). Any solution of the full YBG Eq. (2.2) satisfying these assumptions should be well approximated by some solution of the equation

\[
\frac{d^2 h(r)}{dr^2} + \frac{d-1}{d} \frac{dh(r)}{dr} = \kappa^2 h(r) - \lambda h^3(r)
\]

(2.5)

for \( R_1 < r < \infty \). In Eq. (2.5)

\[
\kappa^2 = \frac{(1 - \mu_0)/\mu_2}{\lambda\rho T} = 1/2w_2
\]

(2.6a)

and

\[
A_{d-1} = \frac{\pi^{(d-1)/2}}{\Gamma\left(\frac{d}{2} + \frac{1}{2}\right)}
\]

(2.6b)

It is straightforward to show that the solutions of Eq. (2.5) for which \( h(r) \to 0 \text{ as } r \to \infty \) always have the form

\[
h(r) = A \frac{\exp(-\kappa r)}{r^{(d-1)/2}}
\]

for \( \kappa > 1 \) and therefore \( \kappa \) is the inverse correlation length (\( \kappa = 1/\xi \)). It is important to note that Eq. (2.5) contains no information about the \( \rho \) or \( T \) dependence either of \( h(r) \) or of the isothermal compressibility \( K_T \), the latter computed from the relation

\[
\rho k_B T K_T = 1 + \rho \Omega_d \int h(r) g^{(1)}(r) \, dr
\]

(2.8)

since the \( \rho \) and \( T \) dependence of \( \kappa \) and \( \lambda \) depend, through Eq. (2.7) on \( g(s) \) for \( s \leq R_0 \) and can only be found from solutions of the full YBG Eq. (2.2). Hence, Eq. (2.5) will give no direct information on exponents such as \( \gamma \) and \( \delta \) which characterize the dependence of \( K_T \) on \( \rho \) and \( T \) in the critical region.

Equation (2.5) does, however, put restrictions on the possible \( r \) dependence of the solutions of the YBG equation satisfying the assumptions made in the derivation of Eq. (2.5). If one assumes that there is a region of \( \rho \) and \( T \) in which \( \kappa \to 0 \) and if one assumes that \( h \) at \( R_1 \)

remains nonzero and finite as \( \kappa \to 0 \), then analysis of Eq. (2.5) shows that: (i) for \( d = 4 \) the correlation \( h(r) \) must become negative for \( r > R_1 \) as \( \kappa \to 0 \), and at \( \kappa = 0 \) the critical correlations behave as \( 2(4-d)/\lambda \) for all \( d < 4 \); and, (ii) for \( d > 4 \), \( h(r) \) has the classical Ornstein–Zernike

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form for $\gamma > R_1$ in the region of small $\kappa$, and at $\kappa = 0$ varies as $1/\gamma^{*\kappa}$ corresponding to a critical exponent $\eta = 0$. These conclusions do not depend on the specific form of the finite range potential $\delta(\gamma)$.

Now the earlier numerical studies of the YBG equation, for a hard-core, attractive, square-well potential and for $d = 3$, appeared to show a region of $\rho$ and $T$ for which $\kappa = 0$ with $h(\gamma)$ remaining positive and slowly varying—in apparent disagreement with (i) above. In this region $K_\gamma$ was found to be characterized by critical exponent values very close to those believed to be correct. It is clear there must be some anomaly here. Perhaps $h(\gamma)$ in the region of small $\kappa$ does not satisfy one or more of the assumptions made in the derivation of Eq. (2.5) so that the equation does not correctly describe the solution of the YBG equation. A second possibility is that there are values of $\rho$ and $T$ for which $\kappa$ is small but no values for which $\kappa = 0$ so that there are “near” critical solutions of the YBG equation which are described well by Eq. (2.5) but no true critical solutions. Finally, it might be that the numerical studies were not done at $\kappa$ small enough to observe the behavior (i) above and that if one constructs numerical solutions near enough to $\kappa = 0$, they will become negative. In addition to these questions one would like, for $d > 4$, to confirm numerically the prediction that the correlations should have the classical Ornstein–Zernike form.

Moreover, the question of the $\rho, T$ dependence of $h(\gamma)$ and $K_\gamma$, and the critical exponents that describe that dependence, remains open. The numerical work described in the rest of this paper was undertaken to answer the above questions.

III. THE NUMERICAL METHOD

The intermolecular potential was taken to be a hard core of unit radius with an attractive square well of radius $R_0 = 1.85$ and depth $\epsilon$. Temperature and density are measured by the parameters $\theta = \epsilon/k_B T$ and $\lambda = \rho \Omega_{\gamma}^{-1}$.

For numerical purposes it is convenient to convert the $\phi$ integral in Eq. (2.2) to the variable $t^2 = \gamma - s^2 - 2 \gamma s \cos \phi$ and to integrate Eq. (2.2) from $r = R$ to $r = \infty$, giving

$$
\ln g(R) = -u(R) + \lambda \int_0^R \int_{r=R}^{r=R_0} \frac{ds}{s} \int_{s}^{2s} \cos \phi (\sin \phi) \gamma^{-1} t \left( g(t) - 1 \right) dt ds dr
$$

(3.1)

where

$$
u(\gamma) = \delta(\gamma)/k_B T \quad \text{and} \quad \cos \phi = \frac{\gamma - s^2 - t^2}{2rs}
$$

For a hard-core attractive square well potential

$$
\frac{ds}{ds} \left( \frac{s}{\gamma} \right) = -\exp(-\theta) \delta(s - R) - \delta(s - 1)
$$

which allows the $s$ integration in Eq. (3.1) to be done and gives

$$
\ln g(R) = -u(R) + \lambda \int_0^R \int_{r=R}^{r=R_0} \frac{ds}{s} \int_{s}^{2s} \cos \phi (\sin \phi) \gamma^{-1} t \left( g(t) - 1 \right) dt ds dr - \lambda g(1)
$$

(3.2)

Equation (3.1) can be exponentiated and written in the form

$$
g(R) = \exp\left(-u(R) + \kappa(R, \{g(v)\})\right),
$$

(3.3)

where $\kappa(R, \{g(v)\})$ is a nonlinear functional of $g(v)$ consisting of the last two terms of Eq. (3.2). The operator $\kappa$ depends on the parameters $\theta$, $\lambda$, and $R_0$.

Equation (3.3) can be exponentiated and written in the form

$$
g(R) = \exp\left(-u(R) + \kappa(R, \{g(v)\})\right),
$$

(3.3)

where $\kappa(R, \{g(v)\})$ is a nonlinear functional of $g(v)$ consisting of the last two terms of Eq. (3.2). The operator $\kappa$ depends on the parameters $\theta$, $\lambda$, and $R_0$.

Now, if $g_n(R)$ is an $n$th order approximation to a solution of Eq. (3.3) then an $(n+1)$th order approximate can be constructed from Eq. (3.3) as

$$
g_{n+1}(R) = \exp\left(-u(R) + \kappa(R, \{g_n(v)\})\right)
$$

(3.4)

in the hope that as $n \to \infty$, $g_n(R)$ converges to a solution of Eq. (3.3). It has long been known empirically, for the $d = 3$ case, that the above iterative process does not converge well for high densities, but that the modified process

$$
g_{n+1}(R) = (1 - \alpha) g_n(R) + \alpha \exp\left(-u(R) + \kappa(R, \{g_n(v)\})\right)
$$

(3.4)

does converge for the parameter $\alpha$ in the range $0.2 \leq \alpha \leq 0.5$, and for well-chosen initial functions $g_0(R)$.

The convergence properties of the iterative process (3.4) and the role of the parameter $\alpha$ will be discussed in some detail in the next section. For the moment it suffices to note that approximate numerical solutions to Eq. (3.3) can be constructed, using the process (3.4) for values of $\lambda$ and $\theta$ in the critical region.

In order to construct such numerical solutions, the continuous variable $1 \leq R < \infty$ must be made discrete and its range must be made finite, i.e., we set $R + \Delta = 1$, $j = 0, 1, 2, \ldots, N$ where $\Delta$ is the grid size and the range is $L = N \Delta + 1$. Physically, we would expect the discrete approximation to Eqs. (3.2) and (3.4) to be accurate if $\Delta$ is chosen small enough that $g(R)$ varies slowly over distances $\Delta$ and so that the integrals in Eq. (3.2) can be done with sufficient precision. Also $L$ should be chosen large enough that the exact boundary condition (2.3) can be approximated by $g(t) = 1$, $t > L$, which is
necessary in order to evaluate the integrals in Eq. (3.2) when \( R \) is near \( L \). For \( L \) large enough, say several times the correlation length, one would expect \( g(R) \), over most of the range of \( R \), to be insensitive to the choice of \( L \) and this is observed to be so. In most of our calculations \( L = 100 \) (the hard-core radius is unity). We have compared calculations done for \( L = 100 \) and for \( L = 110 \) using the boundary condition \( g(L) = 1 \). We have also found solutions to Eq. (3.2) in which we make the range effectively infinite by approximating \( g(R) \) at each iteration by an Ornstein–Zernike form for \( R > 100 \) which matches \( g(L) \).

All of these calculations give, to the accuracy with which we list our results in this paper, the same numerical values for \( g(R) \) for \( 1 \leq R \leq 80 \) and hence we conclude that there is no significant effect of the finite cutoff range on the numerical results.

The choice of grid size \( \Delta \) presents some problems. For \( R \leq 6 \), \( g \) varies fairly rapidly with \( R \). To construct the integrals in Eq. (3.2) to the required accuracy, \( \Delta = 0.025 \) is required. If this grid size is used over the whole range then the iterative process (3.4) must construct \( g \) at about 4000 points per iteration and between 1000 and 2000 iterations are typically required to get sufficiently converged results. The amount of computer time required is prohibitive. For \( R \geq 10 \), on the other hand, \( g(R) \) is so smoothly varying that a grid size of \( \Delta = 0.5 \) provides the necessary numerical accuracy.

Most of our calculations were done on a grid for which \( \Delta = 0.025 \) for \( 1 \leq R \leq 10 \) and \( \Delta = 0.5 \) for \( 10 \leq R \leq 100 \), and thus containing 540 points. The use of two grid sizes causes some technical difficulties in evaluating the integrals in Eq. (3.2) when the point \( R = 10 \) lies inside the region of integration. It is difficult to make firm estimates of the effect of grid size on our numerical results, but again by comparing calculations done with grids of different size we conclude that the effect is negligible to the listed accuracy of our results. Finally, if the calculations are done in double precision, one can show that the accumulated roundoff error is completely negligible (roundoff error is, however, large for single precision calculations).

The above numerical iterative procedure converges rapidly at low density when the initial function \( g_0(R) \) is taken to be the first term in the virial expansion of \( g(R) \). Once a solution to Eq. (3.2) is constructed at a given \( \rho \) and \( T \), either \( \rho \) or \( T \) may be changed slightly and the previous solution used as the initial input for the new iterative process. In this way solutions can be constructed over large portions of the \( \rho, T \) plane. We have, for \( d = 3, 5, \) and \( 6 \), constructed many such solutions and have found, for each dimension, a region of the \( \rho, T \) plane in which \( g(R) \) is long ranged. These solutions are difficult to obtain because the rate of convergence of the iterative process empirically decreases as the range of the solution increases and this ultimately limits our ability to construct very long ranged solutions. We return to this problem and the related problem of estimating errors due to incomplete convergence of the iterative process in the next section.

There are several comparisons between our numerical solutions and the analytic results summarized in

<table>
<thead>
<tr>
<th>( R )</th>
<th>( \kappa_{\text{eff}}(R) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.15</td>
</tr>
<tr>
<td>4</td>
<td>0.17</td>
</tr>
<tr>
<td>6</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Table I: The value of \( \kappa_{\text{eff}}(R) \) vs \( R \), with \( d = 3, \lambda = 4.6; \) \( \kappa = 0.372 \). Here, \( \kappa_{\text{eff}}(R) = -\frac{1}{\gamma(R)} \frac{d\gamma(R)}{dR} - 1/R \).

Sec. II which provides an internal consistency check both on the quality of our numerical solutions and on the validity of the analytic asymptotic approximations. First, either on general physical grounds, or from the differential Eq. (2.5) we expect the numerical solutions to fit the asymptotic form

\[
g(R) - 1 \approx A \exp\left(\frac{\kappa R}{R_a} \right) \quad \text{for } R \geq \kappa
\]

All of our numerical solutions have this form at large \( R \) quite accurately. As an example, in Table I, we consider, for a \( d = 3 \) solution, the behavior of

\[
\kappa_{\text{eff}}(R) = -\left[\frac{1}{\gamma(R)} \frac{d\gamma(R)}{dR} - 1/R \right]
\]

found from the numerical solution for \( g(R) \). If the solution has the above form then \( \kappa_{\text{eff}}(R) \approx \kappa \) for \( \kappa R \gg 1 \).

From the data in Table I we find that \( \kappa_{\text{eff}} \) is constant to better than \( 1\% \) for \( R \geq 40 \) and that \( \kappa 

is typical of all our solutions. It shows that the numerical solutions have the expected behavior at large \( R \) and suggests that \( \kappa \) can be found from this behavior to an accuracy of \( -1\% \).

A second important check is to compare numerical solutions of the full YBG Eq. (3.2) to solutions of the approximate differential Eq. (2.5). Solutions of Eq. (2.5) can be rapidly found to any desired accuracy using standard numerical routines which are not iterative in character and have no associated convergence problems. It is not difficult to devise search procedures which find the solution of Eq. (2.5) which best fits a given numerical solution of Eq. (3.2), say for \( \kappa > R_1 = 10 \). In this fitting procedure one could either use \( \kappa \) and \( \lambda \) in Eq. (2.5) as free parameters in the fit, or fix \( \kappa \) and \( \lambda \) via Eqs. (2.6) and (2.7), from short-range values of the numerical solution of Eq. (3.2). We in fact fix \( \lambda \) but use \( \kappa \) as a fitting parameter for reasons to be discussed shortly (the value of \( \kappa \) found in this way is essentially the same as that found by the method of Table I).

In Table II we show this comparison for \( d = 3, \lambda = 4.60 \) and at two temperatures, for the function \( \gamma(R) - 1/R \). In each case the solutions differ by only one or two in the fifth decimal place for all \( R \geq 10 \). For \( R < 10 \), the assumption that \( g(R) \) is slowly varying, used in the derivation of Eq. (2.5), begins to fail and the difference increases. This comparison is again, typical of all our.
solutions. This excellent agreement is strong evidence that our numerical solutions determine \([g(R) - 1]R\) to about the fifth decimal and that the differential equation is a very good approximation to the full YBG equation for long-ranged solutions.

A third useful comparison is possible since there are two ways to extract the inverse correlation range from the numerical solutions. We can find a \(\kappa_L\) from a long range \((R > 40)\) part of the numerical solutions as indicated in Table I. On the other hand, the analytic results, Eqs. (2.6) and (2.7), provide a value of \(\kappa_L\) depending only on \(g(R)\) at short range [for the hard-core, attractive square well, \(\kappa_s\) depends only on \(g(1)\) and \(g(R_0)\)]. Now \(\kappa_L\) will differ from the true inverse correlation range \(\kappa\) only because of the numerical approximations in our solution of the full YBG equation. However, \(\kappa_L\) will differ from \(\kappa\) both because of numerical approximation and the analytic approximation of the YBG equation by the differential equation (2.5). In Table II we compare \(\kappa_L\) and \(\kappa_s\) for five typical solutions. The difference between \(\kappa_L\) and \(\kappa_s\) is small but perhaps not quite as small as one would expect in view of the extremely good agreement between the numerical solutions of the integral and of the differential equation, shown in Table II.

One can show that the principal effect of keeping higher-order terms in the derivatives of \(g(R)\) in the derivation of the differential equation is to give small corrections to the formula (2.8) for \(\kappa_s\). These corrections are of order 1% and will decrease the difference between \(\kappa_L\) and \(\kappa_s\) shown in Table III. The remaining difference, while small, is still slightly larger than we can completely account for by various ways of estimating residual errors. It is, however, difficult to make firm error estimates in our numerical procedure so it is not clear if the above difference indicates some small inadequacy in our numerical procedures. These three comparisons, nevertheless, are good enough to warrant considerable confidence both in the accuracy of our numerical solutions and the approximations of the analytic studies and results of Sec. II.

The numerical solutions constructed by the above method for \(d = 3\), 5, 6 have, for each \(d\), a region of density and temperature in which they become long ranged. The region of the \(\lambda, \theta\) plane inside which the correlation range \(\xi = \kappa^{-1}\) of the solutions is large, say greater than seven hard core radii, is shown by the dashed line in Fig. 1. The apex of this region occurs roughly at \(\theta \approx 0.37\), \(\lambda \approx 4.6\) for \(d = 3\), at \(\theta \approx 0.09\), \(\lambda \approx 15\) for \(d = 5\), and at \(\theta \approx 0.05\), \(\lambda \approx 24\) for \(d = 6\). As one moves into the region shown in Fig. 1 the correlation range of the solutions increases and the convergence rate of the iterative numerical process slows so that solutions are more difficult to construct. The earlier \(d = 3\) numerical study\(^6\) seemed to indicate the existence of a stability line (the solid line in Fig. 1) at which the correlation range became infinite (i.e., \(\kappa = 0\)). The central problem is to find this stability line, if it exists.

### Table III. Comparison of inverse correlation ranges extracted from short-range data \(\kappa_s\) and from long-range data \(\kappa_L\) for \(d = 3\), \(\lambda = 4.5\), 60.

<table>
<thead>
<tr>
<th>(\theta)</th>
<th>(\kappa_s)</th>
<th>(\kappa_L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.369</td>
<td>0.153</td>
<td>0.149</td>
</tr>
<tr>
<td>0.370</td>
<td>0.135</td>
<td>0.131</td>
</tr>
<tr>
<td>0.371</td>
<td>0.117</td>
<td>0.113</td>
</tr>
<tr>
<td>0.3715</td>
<td>0.109</td>
<td>0.105</td>
</tr>
<tr>
<td>0.372</td>
<td>0.102</td>
<td>0.097</td>
</tr>
</tbody>
</table>
and to investigate the behavior of \( g(R) \) in its vicinity. The major difficulty is that the convergence rate of the iterative process appears to approach zero as \( \kappa < 0 \) (or at least near \( \kappa = 0 \)) so one cannot construct solutions arbitrarily close to the stability line. In constructing these long-range solutions, therefore, it is essential that one be able to distinguish between slowly convergent iterative processes and nonconvergent processes. We take up this question in the next section.

IV. CONVERGENCE OF FIRST-ORDER ITERATIVE PROCESSES

We write the YBG Eq. \((3,3)\) in fixed point form as

\[
\{ g(r) \exp[-i \theta(r)] + S' \}
\]

Here \( S \) is a nonlinear operator on some linear space of functions. We shall assume in the following discussion that \( S \) has certain properties that, in general, are very difficult to prove—and no attempt to do so will be presented here. We shall see, however, that these assumed properties give rise to a sensible and accurate description of the observed behavior of our iterative process and provide a natural way to understand that behavior.

The basic question to be addressed here is: Under what conditions will the iterates \((r)\) given by

\[
\{g(r) = (1 - \exp(-i \theta(r))) S' g(r)\}
\]

converge to a solution \( g(r) \) of Eq. \((4,1)\) as \( n \to \infty \)? It is difficult to give a global answer to this question for arbitrary initial functions \( g_0(r) \); however, a local discussion is possible. Suppose \( g_0(r) \) is "close" to a solution \( g(r) \) of Eq. \((4,1)\) so that

\[
\lambda = n \in \mathbb{R} \quad \text{and} \quad g_n(r) = g(r) + \sum_k \frac{\lambda^k}{k!} g_k(r)
\]

is "small". We expand Eq. \((4,2)\) in a functional Taylor's expansion about the solution \( g(r) \), to first order in \( g_n(r) \), to obtain

\[
\delta g_n(r) = S'\{g(r)\} \delta g_n(r)
\]

where the \( \delta g \) are elements of some linear vector space of functions and \( S' \), the functional or Fréchet derivative of \( S \), is a linear operator on that space, i.e., \( S' \), evaluated at the fixed point \( g(r) \) of Eq. \((4,1)\), is a fixed linear operator on \( \delta g(r) \). In the case of the YBG equation \( S' \) is a linear integral operator of rather complex structure. We assume that \( S' \) has a complete set of linearly independent eigenfunctions \( \phi_\alpha(r) \), i.e.,

\[
S' \phi_\alpha(r) = \lambda \phi_\alpha(r)
\]

so that for each \( n \) we can expand

\[
\delta g_n(r) = \sum_\alpha c_\alpha \phi_\alpha(r)
\]

where \( \phi \) runs over the indexed set of eigenfunctions of \( S' \). Substituting the expansion \((4,4)\) into the relation \((4,3)\) gives the simple recursion relation

\[
a_{n+1,\alpha} = c_\alpha a_{n,\alpha}
\]

which has the solution

\[
a_{n,\alpha} = (c_\alpha)^n a_{0,\alpha},
\]

where the \( a_{n,\alpha} \) are the expansion coefficients of the function

\[
\delta g_n(r) = g_n(r) - g(r)
\]

Therefore, in this linear approximation the iterates

\[
\delta g_n(r) = \sum_\alpha (c_\alpha)^n a_{0,\alpha} \phi_\alpha(r)
\]

We see that if

then the iterative process will converge locally, i.e., for any initial function \( g_0(r) \) near enough to the solution \( g(r) \) that the linear approximation \((4,3)\) is valid. If, however,

\[
\max_\alpha |c_\alpha| >
\]

then the process will diverge for some \( g_0(r) \). Finally

\[
\max_\alpha |c_\alpha| = 1,
\]

the convergence or divergence of the process depends on higher-order terms in the expansion of \( S' \).

We can now easily see the role of the parameter \( \alpha \) in the modified iterative process \((3,4)\). Suppose \( S' \) has bounded spectrum with

\[
\max_\alpha |c_\alpha| <
\]

so that the process \((4,2)\) diverges. Equation \((4,1)\) can be rewritten as

\[
g(r) = (1 - \alpha) g(r) + \alpha S'\{g(r)\}
\]

which suggests the iterative process

\[
g_{\alpha+1}(r) = S_\alpha\{g_\alpha(r)\}
\]

where

\[
S_\alpha = (1 - \alpha) I + \alpha S'
\]

Now, the solutions of Eqs. \((4,1)\) and \((4,7)\) are the same but the corresponding iterative processes \((4,2)\) and \((4)\) are not. The convergence of the modified process \((4)\) is determined by the eigenvalues of the derivative operator \( S'_\alpha \). Since \( S_\alpha \) and \( S' \) differ by a multiple of the identity operator, the eigenvalues of the derivative operators \( S'_\alpha \) and \( S' \) are related by

\[
c_\alpha(\alpha) = (1 - \alpha) + \alpha c_\alpha.
\]

Under some, but not all, circumstances a proper choice of \( \alpha \) will make the modified process converge when the original process does not. For example, if the divergence is due to eigenvalues with negative real parts then a small positive value of \( \alpha \) will make the process converge. Note, however, that if the original process has an eigenvalue with real part greater than or equal to one, then so does the modified process for any \( \alpha > 0 \) and therefore both will diverge. In practice the modified process with \( \alpha \leq 0.5 \) converges for the YBG equation.

A particularly simple pattern of convergence emerges if the eigenvalue \( c_0 \) of largest amplitude is discrete and nondegenerate. For \( n \) large enough the \( \beta = 0 \) term will dominate all others in Eq. (4.6). Then the \( n \)th iterate behaves as
\[ g_n(r) = g(r) + (c_0^n) a_n \phi_0(r) + \cdots. \]

Since \( g(r) \) is unknown it is convenient to consider the difference between successive iterates
\[ \Delta_n(r) = g_n(r) - g_{n-1}(r) = c_0^n \left( 1 - \frac{1}{c_0} \right) a_n \phi_0(r) + \cdots. \]  

(4.10)

For the YBG equation the sequence \( \Delta_n(r) \) is monotone indicating that \( c_0 > 0 \). If \( c_0 < 0 \) the sequence would alternate in sign.

The most characteristic property of this simple case is that the rate of convergence is determined by \( c_0 \) and is the same for all \( r \) for large \( n \).

From Eq. (4.10) we have
\[ \ln |\Delta_n(r)| = n \ln |c_0| + \ln \left| 1 - \frac{1}{c_0} \right| a_n \phi_0(r) \]

(4.11)

so a plot of \( \ln |\Delta_n(r)| \) vs \( n \) for several \( r \), should be a set of parallel straight lines of slope \( \ln |c_0| < 0 \) and whose intercepts are related to the eigenfunction \( \phi_0(r) \) of the linearized operator. Table IV and Fig. 2 give the behavior of \( \ln |\Delta_n(r)|/n \) for \( d = 3 \), \( \lambda = 4.60, \theta = 0.3741 \), and for several values of \( r \). The points fall quite accurately on parallel straight lines whose slope gives a value \( c_0 = 0.9965 \). Also shown is a similar plot for the compressibility iterates which, as integrals of \( g_n(r) \), have the same convergence properties. For this simple kind of convergence the error \( \delta g_n(r) \) remaining after \( n \) iterations can be estimated from the result
\[ \ln |\Delta_n(r)| = n \ln |c_0| + \ln \left| 1 - \frac{1}{c_0} \right| a_n \phi_0(r) \]

(4.12)

For slowly convergent processes with \( c_0 \approx 1 \) the error \( \delta g_n \) is much larger than the difference \( \Delta_n \) between successive iterates. As an example, from Table IV, for \( r = 1.85, n = 1200 \) we have \( \Delta_{1200}(1.85) = 6.713 \times 10^{-10} \), whereas \( \delta g_{1200}(1.85) = 3.7 \times 10^{-10} \). For slowly convergent processes an analysis of this kind is important. Without some understanding of the rate of convergence there is no relationship between \( \Delta_n \) and the remaining error. It is possible for the \( \Delta_n \) to decrease slowly to zero even for a divergent process so iterations carried out until \( \Delta_n \) is very small do not necessarily have small remaining error.

The above simple description of convergence applies to all of the solutions we have constructed. The convergence of the iterative process is dominated by a real, discrete, nondegenerate eigenvalue \( c_0 \) which is close to unity for long range solutions. In fact, empirically, the eigenvalue \( c_0 \) extracted from the convergence plots seems to approach unity at or near points where \( \kappa \) becomes zero. In Table V and Fig. 3 we show, for \( d = 5 \), the observed behavior of \( c_0 \) and \( \kappa \) along an isochore and an isotherm. Figure 3 suggests that, in each case, \( c_0 - 1 \) as \( x \rightarrow 0 \), though not at the same rate, and the scatter of the points is enough to suggest that \( c_0 \) might have a weak dependence on parameters other than \( x \). This relationship between \( c_0 \) and \( \kappa \) is of some interest. It is known that a necessary condition for a bifurcation of solutions of a large class of nonlinear integral equations is that an eigenvalue of the derivative operator approaches unity. If the eigenvalue is of odd multiplicity then this condition is also sufficient. Thus, the above data for the YBG equation strongly suggests that the stability
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The differential equation analysis, that the critical correlations in \( d = 3 \) (if they exist) must be negative (and hence unphysical), does not apply.

In contrast to the case \( d = 3 \) described above, for the dimensions \( d = 5, 6 \) we find a well-defined stability line in the liquid–gas regime. If we move into the region long-ranged solutions, say along an isochore (fixed \( \kappa \) continues to decrease with no sign of a minimum), appears to extrapolate to zero at a stability temperature \( \theta(\lambda) \), which determines the stability line. This extrapolation is made by fitting the \( \kappa \) vs \( \theta \) data to the form

\[
\ln \kappa = \ln A + \nu \ln \left( \frac{\theta(\lambda)}{\theta} - 1 \right).
\]

The data for seven isochores are given in Table VI and the corresponding values of \( \nu \) and \( \theta(\lambda) \) are shown in Table VII. The values of \( \kappa \) in Table VI are found from numerical solutions using the short range formulas, Eqs. (2.6) and (2.7). The numerical solutions again satisfy all of the consistency and convergence checks although the convergence rate is very slow \( (c_0 \approx 0.99) \) for the solutions with the smallest \( c_0 \)'s. The exponent so determined is nearly independent of \( \lambda \) and is very close to \( 1/2 \). The stability curve itself can be found fitting the seven values of \( \theta(\lambda) \) vs \( \lambda \). We again point out that this stability line is determined by extrapolation of \( \kappa \) to zero. We cannot construct solutions with \( \kappa \leq 0 \) because of the slowness of convergence of the iterative procedure. But, in contrast to the case \( d = 3 \), we can construct no solutions inside the stability line so determined for \( d = 6 \). If we try to construct solutions very near the stability line, or anywhere inside of it, the iterative process is apparently well behaved for 100 or 200 iterations, during which the \( \kappa^2 \) [computed from the short-range values of \( g(r) \)] drifts toward zero. At some point in the iterations \( \kappa^2 \) becomes negative and the process then begins to diverge catastrophically. Thus, it appears that there is a line in the \( (\lambda, \theta) \) plane where \( \kappa \) and that inside that line the largest eigenvalue of the

V. RESULTS AND CONCLUSIONS

In this concluding section we summarize the principal results obtained in our study of the YBG equation (assuming the Kirkwood superposition closure), and discuss their significance in light of current theories of critical phenomena and phase equilibria. For \( d = 3 \) our conclusion is that the pair correlation function data generated from the YBG equation do not exhibit the long-range correlations necessary for existence of a true stability line in the liquid–gas regime. There is a region of \( \lambda \) and \( \theta \) near \( \lambda \approx 4.60 \) and \( \theta \approx 0.37 \) where the solutions are long ranged (\( \kappa \) is small), but for all these solutions \( \kappa \) (while small) remains greater than zero throughout the region. The correlations of longest range have \( \kappa \approx 0.08 \) (\( \lambda \approx 12.5 \)) and occur very near \( \lambda, \theta \) \( \approx (4.60, 0.375). \) Here the convergence rate of the iterative process is slow \( (c_0 \approx 0.997) \), but very stable. These solutions satisfy all the consistency checks described in Sec. III and we believe there is no reason to doubt their accuracy. Given the nonzero minimum value of \( \kappa \) determined in our studies, critical correlations \( (\kappa = 0) \) never develop for the \( d = 3 \) case, and hence no stability line is present. Thus, the requirement from

FIG. 3. A plot of the logarithm of the correlation function \( \xi (\kappa^2) \) vs the logarithm of the convergence rate, \( \ln(1 - c_0) \), for data along the \( d = 6 \) critical isotherm (circles) and along the critical isochore (triangles).
This form gives the values $\theta_e = 0.0458677$, $\lambda_e = 23.9572$, $C = 1.97685 \times 10^{-4}$, and $D = 130.9$ with the average error in the fit about 1%. This fit is probably slightly better than the accuracy to which $\kappa^2$ is determined from the short-range values of $g(r)$. The large number of significant figures in the constants $\theta_e$, $\lambda_e$, and $C$ are necessary because of large cancellations between the two terms in the above expression for $\kappa^2$. The data of Table VIII, obtained from 21 solutions for $d = 5$, can also be fit with this form; with the values $\theta_e = 0.0904008$, $\lambda_e = 15.0785$, $C = 1.23373 \times 10^{-4}$ and $D = 56.51$, the fit to $\kappa^2$ has an average error of 0.2%. Note that functional form assumed above for $\kappa^2$ implies that the critical exponent $\nu$ defined by

$$\kappa(\theta_e, \lambda_e) = C(\lambda - \lambda_e)^{2\nu}$$

has the mean field value of 1/2 (exactly). To find the equation for the stability curve we set $\kappa^2 = 0$ and solve for $\theta$, giving

$$\theta(\lambda) = \theta_e + C(\lambda - \lambda_e)^{2\nu}$$

This equation fits the data of Table VII to the sixth decimal place and provides something of a check on the fitting procedures. On the stability line the compressibility becomes infinite; hence it is analogous to the spinoidal line of the van der Waals mean-field theory and has the same quadratic dependence on density. It is natural to identify the lowest point $(\theta_e, \lambda_e)$ on the stability line as the critical point although, strictly speaking, all points on the stability line generated by the YBG equation are equally "critical" and, in fact, one could write the same homogeneous form for $\kappa^2$ relative to any point on the stability line by using appropriately rotated variables.

The isothermal compressibility $K_T$ can be found [Eq. (2.8)] by a numerical integration of $h(r) = g(r) - 1$. An
interesting prediction of the analytic studies is that for $d > 4$, $K_T$ should be proportional to $k^2$ near the stability line. In Tables IX and X are shown the product $K_T k^2$ for nine $d = 6$ solutions (four near the critical isotherm and five near the critical isochore) where $k$ is again determined from Eqs. (2.6) and (2.7). This product appears to approach the value $1.36$ near the critical point. This relation between $K_T$ and $k^2$ implies the mean field form

$$K_T = A \left( \quad \right)$$

for the compressibility and the classical values $\delta = 3$, $\gamma = 1$ for these critical exponents. There is no way within the YBG theory to determine directly the coexistence boundary between the stable one-phase and stable two-phase states. This boundary presumably lies outside the stability line and is tangent to it at $(\lambda, \theta)$. If this is so then the equation for the coexistence curve would, with the above form for $K_T$, determine the exponent $\gamma'$ characterizing the behavior of $K_T$ with $\theta$ along the coexistence curve. If we assume a quadratic coexistence curve

$$\theta = C' (\lambda - \lambda_c)^2$$

with $C' < C$, then $\gamma' = 1$.

The numerical results described in this paper show convincingly that, at least for the square-well potential, the YBG equation has no critical behavior for $d = 3$ and has mean field critical behavior for $d = 5, 6$. These calculations also confirm the appropriateness of the approximate differential equation and the results derived from it. Taken together the numerical and analytic studies strongly suggest that, for any short-range potential, the YBG equation has no critical behavior for $d \leq 4$ and has mean field critical behavior for $d > 4$. This general conjecture can, of course, only be supported, not proven, by numerical methods. It is conceivable, for example, that a somewhat longer-range potential would produce a stability line for the $d = 3$ case. We think this unlikely but were it to occur we would expect the resulting solutions still to be described by the differential equation. No realistic critical behavior for $d < 4$ is compatible with this differential equation [Eq. (2.5)] which appears to be an excellent approximation to the full YBG equation in the region of long-ranged solutions. In the end, however, final proof of the correctness of our picture of the critical behavior of the YBG equation awaits the development of analytic techniques of sufficient sophistication to deal with the full YBG equation.

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8. Note that for the $d = 3$ case, $\lambda = \lambda_c/2$, where $\lambda_c$ is the density parameter used in the calculations of Refs. 4 and 6.