Se describe un procedimiento particularmente eficiente y versátil para la solución numérica de las ecuaciones integrales no-lineales que gobiernan la estructura microscópica de los fluidos. Se utilizan funciones lineales simples que son sólo distintas de cero sobre elementos finitos. Estas funciones, que en conjunto cubren el dominio de las soluciones, simplifican notablemente el tratamiento de las no-linearidades. Este método ha sido usado previamente para resolver ecuaciones no-lineales como las de Percus-Yevick, HNC y la de la aproximación esférica promedio (MSA). En este artículo ilustramos su aplicación en la determinación de los exponentes críticos \( \gamma \) y \( \delta \) de la transición líquido-vapor en la MSA para un fluido de esferas duras con una parte atractiva con forma de Yukawa. Presentamos una comparación de los resultados obtenidos para \( \gamma \) y \( \delta \) a partir de las soluciones numéricas y analíticas de MSA para ese sistema. Esa comparación nos permite clarificar algunas de las limitaciones que tienen los métodos numéricos comúnmente disponibles cuando se pretende usarlos en la determinación de la posición del punto crítico y los exponentes críticos correspondientes.
ABSTRACT

A particularly efficient and versatile procedure for numerically solving the nonlinear integral equations governing fluid microstructures is described here. Simple linear basis functions are used on finite elements that collectively span the solution domain and simplify the treatment of nonlinearities. The method has been used before for solving nonlinear integral equations like Percus-Yevick, HNC, and mean spherical approximation (MSA). In this paper we illustrate its application to the determination of the critical exponents $\gamma$ and $\delta$ of the liquid-vapor first order phase transition in the MSA for a fluid of hard spheres with a Yukawa tail. We present a comparison of the results obtained for $\gamma$ and $\delta$ from numerical and analytical solutions of the MSA for that system. That comparison allows us to clarify some of the limitations in the currently available numerical methods for the correct determination of both the position of the critical point and the corresponding critical exponents.

1. INTRODUCTION

The microscopic structure of a simple liquid in equilibrium is defined by the probability densities of finding two, three or more particles at specified locations in space\cite{1,2}. The radial distribution function $g(r)$ is of capital importance in the determination of both the structure and the thermodynamics of the fluid. For spherical molecules $g(r)$ is a function of the distance $r$ alone and can be determined experimentally from neutron or X-ray diffraction experiments\cite{3}. The pair distribution function $g(r)$ approaches unity as $r$ becomes large. On the other hand, for pair potentials which are strongly repulsive at short distances, one particle excludes other particles from its immediate neighborhood and $g(r) \to 0$ as $r \to 0$. It is customary to define the direct correlation function $c(r)$ by means of the Ornstein-Zernike\cite{4} (OZ) equation,

$$ h(r) = c(r) + \rho \int g(s) h(s) c(|r - s|) \, ds, \tag{1} $$

where $h(r) = g(r) - 1$ is called the total correlation function and $\rho$ is the number density of particles in the system. The function $c(r)$ has a shorter range than $g(r)$ and a simpler form. Several approximations have been proposed for the calculation of the functions $c(r)$ and $h(r)$, from the OZ equation (1). Three widely studied approximations\cite{1,2}, which result in nonlinear integral equations for $g(r)$ or $c(r)$ are the
Percus Yevick (PY) approximation\(^5\),

\[ c(r) = g(r) \left( 1 - \exp(\beta \phi(r)) \right), \quad (2) \]

where \( \beta = 1/kT \), the hypernetted chain (HNC) approximation\(^6\),

\[ c(r) = g(r) - 1 - \ln g(r) - \beta \phi(r), \quad (3) \]

and the mean spherical approximation\(^7\) (MSA),

\begin{align*}
  h(r) &= -1 \text{ for } r < \sigma, \\
  c(r) &= -\beta \phi(r) \text{ for } r > \sigma.
\end{align*} \quad (4)

In this form, the MSA is only applicable to potentials with a hard core diameter \( \sigma \). In the last three equations \( \phi(r) \) denotes the intermolecular pair potential, \( k \) Boltzmann's constant, and \( T \) absolute temperature. These nonlinear equations are usually solved numerically either by direct iteration\(^8\) or through a double Fourier transform scheme\(^8\). Some other methods use the expansion of the correlation functions in a set of basis functions\(^9\). The coefficients of the expansion are found by executing some scheme for reducing a measure of the error of approximation to a prescribed level. This procedure results in a set of nonlinear algebraic equations which are solved commonly by Picard iteration\(^10\).

Many of the published algorithms for solving these nonlinear integral equations require numerous iterations and thus large amounts of computational work. Moreover, they have difficulty in converging on solutions for certain states of physical interest like metastable and unstable fluid states, or states in the neighborhood of the critical point. The domains of convergence of solutions that have been found are neither documented, nor it is known whether these solutions are unique. In a recent paper\(^11\), an efficient and versatile numerical method for solving nonlinear integral equations of the second kind\(^12\)
was presented. The method opens the way to investigate systematically the solution spaces of such equations, e.g., by surveying domains of convergence, by analyzing bifurcation behavior, and by following multiple solution families as parameters are varied. The key to the method is the use of simple basis functions from finite element analysis that are nonzero only in small domains but collectively span the entire spatial domain of the problem. The coefficients of such finite elements expansion are the local values of the expanded functions, a situation not generally occurring in traditional Fourier expansions in terms of globally defined basis functions. Collocation weighted residuals are employed to minimize the error of approximation and the resulting set of equations is solved by Newton iteration.

This finite element computational method has been applied to PY and HNC integral equations for a 6-12 Lennard-Jones fluid. In order to study the type of correlation functions predicted by the PY integral equation inside the liquid–vapor coexistence curve, Mier y Terán et al. found continuous isothermal solution branches crossing the two phase region from vapor to liquid densities. In Fig. 1, the negative of the direct correlation function at \( r=0 \), \(-c(0)\), is plotted versus density. For certain temperatures, lower than critical, the isotherm follows a path of increasing density until a turning point in the density is reached, and then turns back to low densities. A second turning point in density is then reached, and the solution branch follows again a path of increasing density up to liquid state densities. Thus, the solution space of the PY equation bifurcates as the three-solution density interval is approached from the vapor or the liquid side. The solution space found for the PY equation differs from the solution space determined by Watts for a truncated Lennard-Jones 6-12 potential. The differences were attributed to the Baxter transformation, which Watts employed. The finite element approach was also used by Quiñones for solving the MSA for the square-well fluid. More recently, Kerins et al. used the same finite element
Fig. 1. Isotherm of $-c(0)$ versus density, $\rho \sigma^3$, for the PY integral equation with a Lennard-Jones (6-12) potential for the subcritical temperature $T/\varepsilon = 1.25$. There is a density interval over which $-c(0)$ is a triple-valued function of density. In this figure, $\sigma$ and $\varepsilon$ are the Lennard-Jones parameters.
technique to study the liquid-vapor coexistence region of a truncated and shifted 6-12 Lennard-Jones fluid for the PY and HNC integral equations, and for the Born-Green-Yvon integrodifferential equation under the Kirkwood superposition approximation.

In all the cases mentioned, the rapid convergence found (less than five iterations even in the neighborhood of spinodal curve) contrasts with that of the traditional Picard method for which hundreds of iterations are necessary to obtain solutions of similar accuracy.

The main purpose of this work is to illustrate the use of the finite element method for integral equations with a numerical study of the critical behaviour of the hard core Yukawa fluid (HCYF) in the mean spherical approximation. MSA is analytically solvable for the HCYF, a simple model fluid in which particles interact with the spherically symmetric pair potential

\[ \phi(r) = \begin{cases} \infty & r < \sigma \\ -\left(\frac{\varepsilon}{r}\right)\exp\left[-\zeta(r - \sigma)\right] & r > \sigma, \end{cases} \]

where \( \sigma \) is the diameter of the hard core, \( \varepsilon \) is the depth of the attractive well, and \( \zeta \) is a parameter related with the rate of decay of the potential. In an earlier work, Stell\(^{21}\) showed that, provided the interactions were sufficiently short ranged, a class of approximations including MSA should exhibit spherical model critical exponents (see Table 1) from the compressibility equation of state; that is, the equation of state obtained from

\[ B \equiv \left(\frac{\partial \rho}{\partial \rho}\right)_T = 1 - \rho \int c(r)dr, \]

where \( B \) is a dimensionless isothermal bulk modulus. This result was later confirmed by Cummings and Stell\(^{22}\) for the HCYF. The idea behind this study is to test the finite element numerical technique, which has proven to be so efficient and stable in the situations...
TABLE I

Definition of the critical exponents $\gamma$ and $\delta$ in terms of the isothermal compressibility $K_T$, $\rho K_T = (\partial \rho / \partial T)_T$ and the quantities $\Delta \rho = \rho - \rho_c$ and $\Delta T = T - T_c$. The mean field classical values (MF), the spherical model values (SM) and the experimental values\textsuperscript{31} for real systems are shown.

<table>
<thead>
<tr>
<th>Exponents</th>
<th>Definition</th>
<th>MF</th>
<th>SM</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td>$K_T \sim \Delta T^{-\gamma}$ $\rho = \rho_c$, $T = T_c$</td>
<td>1</td>
<td>2</td>
<td>1.24 ± 0.05</td>
</tr>
<tr>
<td>$\delta$</td>
<td>$K_T \sim</td>
<td>\Delta \rho</td>
<td>^{1-\delta}$ $T = T_c$</td>
<td>3</td>
</tr>
</tbody>
</table>

described previously, in the determination of the critical exponents $\gamma$ and $\delta$ of the HCYF.

Because solving Eq.(1) on an unbounded domain is impracticable, an asymptotic condition must be imposed on the function $h(r)$. That is, $h(r)$ is required to take on an asymptotic form at large values of $r$. The option most frequently used, is simply to assume that the total correlation function vanishes for $r$ greater than a cut-off value, $R$. Watts\textsuperscript{14} avoided to impose this restriction using a form of the PY equation derived by Baxter\textsuperscript{15}. In this work, we truncated the correlation function for distances longer than $R = 6\sigma$. The cut-off value, $R$, has important consequences on the values obtained for both the location of the critical point and the critical exponents. It is a main conclusion of this work that a too short truncation of the function $h(r)$ yields values for the critical exponents which are consistent with mean field values.
In section 2 we give a brief outline of the numerical method used. We next describe in section 3 the procedure for determining the location of the critical point from the analytic solution of MSA for the HCYF. In section 4 we describe the procedure followed in order to do a numerical determination of both the critical point and the critical exponents $\gamma$ and $\delta$. Finally, in section 5, we discuss our results in relation with the truncation of the correlation function $h(r)$.

2. FINITE ELEMENT METHOD

In order to obtain correlation functions from the MSA, Eq. (1) coupled with Eqs. (4) must be solved. Integrated over the azimuthal angle, Eq. (1) becomes

$$h(r) = c(r) + 2\pi \rho / r \int_0^\infty ds c(s) \int_{|r-s|}^{r+s} dt \phi(t).$$  (7)

With the definitions

$$C(r) = r \ c(r),$$  (8)

$$h(r) = r \ h(r),$$  (9)

and the substitution of the closure condition given by the MSA, Eq. (7), becomes

$$-r = C(r) + 2\pi \rho \left\{ \int_0^1 ds C(s) \int_{|r-s|}^{r+s} dt \phi(t) 
- \int_1^\infty s \delta(s) \int_{s-r}^{r+s} dt \phi(t) \right\} \quad (r \leq a),$$

and
\[ H(r) = -r \beta \phi(r) + 2 \pi \rho \left\{ \int_0^1 ds \, C(s) \int_0^1 ds \, \frac{r+s}{r-s} dt \, H(t) \right\} \quad (r \geq \sigma). \quad (10) \]

In Eqs. (10), lengths are scaled by the diameter \( \sigma \). Correspondingly, \( \rho \) represents the number density reduced with \( \sigma \). We shall use reduced units throughout the paper.

The goal of the finite element method is to reduce a single equation, \( L(y) = 0 \), to a system of algebraic equations by subdividing the domain of the problem into a number of subdomains of appropriate size and shape and representing the solution by a simple form over each subdomain or element. Thus, the unknown solution \( y(r) \) is approximated by a set of linearly independent basis functions \( \{ \psi_j \} \),

\[ y_{\text{approx.}}(r) = \sum_{j=1}^{N} q_j \psi_j(r), \quad (11) \]

the unknown coefficients of which, \( \{ q_j \} \), are the values of the solution at the intersections or nodes of the elements.

In the collocation version of the method of weighted residuals\(^{13} \), the residual function \( L(y_{\text{approx.}}) \), is reduced to zero at the nodes of the elements:

\[ \int_V L(y_{\text{approx.}}) \delta(r - r_i) d^3r = 0, \quad (12) \]

for \( i = 1, \ldots, N \), where \( \delta(r - r_i) \) is the Dirac delta function.

As we mentioned before, to solve Eqs. (10) we truncated the correlation functions at \( r = R \). The domain \( 0 \leq r \leq R \) was divided into an even mesh of 120 nodes. As the basis functions we chose a set of polynomials or "chapeau" functions defined by
\[
\psi^j (r) = \frac{(r - r_{j-1})}{(r_j - r_{j-1})}, \quad r_{j-1} \leq r_j \leq r_j
\]

\[
= \frac{(r_{j+1} - r)}{(r_{j+1} - r_j)}, \quad r_j \leq r \leq r_{j+1}
\]

\[
= 0, \quad \text{otherwise},
\]

where \( r_j \) is the value of \( r \) at the \( j \)-th node. As a consequence of the MSA closure condition, Eq. (4), the unknown functions in our case are \( c(r) \) for \( 0 \leq r \leq 1 \), and \( h(r) \) for \( 1 \leq r \leq R \).

The set of non-linear algebraic equations for the unknown coefficients was solved by Newton's method\(^2\), which provides a set of linear equations for the expansion coefficients at the \((n+1)\)-st iteration in terms of the coefficients at the \(n\)-th iteration. In compact notation:

\[
J(q^n) \cdot q^{n+1} = F(q^n),
\]

where \( J \) is the Jacobian matrix of the algebraic system \( F(q) \). We invert this matrix by Gauss elimination to find \( q^{n+1} \). The Newton process is continued until the Euclidean norm of the difference between successive iterations becomes less than a prescribed small number \( \Delta \):

\[
\| q^{n+1} - q^n \| \equiv \left[ \sum_{j=1}^{N} (q^{n+1}_j - q^n_j)^2 \right]^{1/2} \leq \Delta.
\]

Critical to Newton's method is the initial estimate to the solution profile, \( q^0 \), which must be accurate enough to fall within the method's domain of convergence around the solution sought. In general, finding a good initial guess can be difficult. Often it is helpful to find a solution for a set of parameters or conditions for which either a conventional analytic solution or an asymptotic approximation is known. Once the first solution is obtained, results for other parameter
values usually can be found easily by a continuation technique such as the first-order one described below. In the present case, we choose to obtain a solution by selecting a value of the density \( \rho \) for which the low density limit, \( c(r) = -1 \) for \( 0 \leq r \leq 1 \), and \( h(r) = 0 \) for \( r \geq 1 \) is a good approximation to the solution. Once a solution is found for these conditions, initial estimates for solutions at other values of the density along a given isotherm are obtained by a first-order continuation technique similar to Euler's method. Initial estimates for other densities are generated from the converged Jacobian \( J(q_s, \rho_s) \) of the previous solution \( q_s \) at \( \rho_s \) by expanding in a Taylor series in density:

\[
J(q_s; \rho_s) \cdot (q - q_s) = -\frac{\partial F}{\partial \rho} \cdot (\rho - \rho_s).
\]  

(15)

Such continuation can also be performed for variations in other parameters, such as the temperature or the parameters in the intermolecular potential.

The continuation technique generalizes to incorporate turning points in the solution. Near a turning point, changes in some of the expansion coefficients become extremely sensitive to small changes in the parameter which is varied independently. This behaviour can result in a divergent iteration. The difficulty associated with the turning point is removed by an interchange between the parameter and the expansion coefficient that is most sensitive to changes in that parameter\(^2\). The parameter thus becomes a dependent variable and the expansion coefficient is transformed into an independent parameter.

3. ANALYTICAL CALCULATION.

Waisman\(^1\) solved analytically the MSA for the HCYF. His solution, given in the form of a set of nonlinear algebraic equations, was later simplified by H"{o}ye and Stell\(^2\). The value of the isothermal bulk modulus, \( B \), can be determined by solving for \( B \), \( b \) and \( v \) - the following set of equations:
\[ A = p - U_0 - \frac{1}{2}(p - \xi \sqrt{A}) + \frac{1}{2}(P_0^2 + 2P_0 \xi \sqrt{A} + P_0^2)^{12}, \quad (16) \]

\[ y_0 = (A + U_0 - 1)/6 \xi, \quad (17) \]

\[ 24\xi y^2 = -4b + 2v\xi - v^2/K \exp(\xi), \quad (18) \]

where \( K \equiv \xi/kT; \xi = \pi p/6; A = B(1 - \xi)^2; \]

\[ P = (1 + 2\xi)^2/(1 - \xi)^2; \quad \sigma_0 = [(\xi - 2)/(\xi + 2) + \exp(-\xi)]/2\xi; \]

\[ U_0 = (6\xi/K)(\xi + 2)^2(K - \sigma_0 v)/\xi^2; \]

\[ y_0 = K + (\xi/2 + 1)B + b + v(1 - \exp(-\xi))/\xi \]

\[ + v^2 \cosh(\xi)/2K\xi^2 \exp(\xi). \]

Once that the Eqs. (16-18) are solved for particular values of temperature and density, the direct correlation function, \( c(r) \), can be obtained from

\[ -c(r) = B + br + \frac{1}{2}\xi Br^3 + v(1 - \exp(-\xi))/\xi r \]

\[ + v^2(\cosh(\xi r) - 1)/2K\xi^2 \exp(\xi) r, \quad r < 1. \quad (19) \]

Equations (16) and (17) were obtained by Høye and Stell\textsuperscript{20} by algebraic manipulation of the original Waisman's equations\textsuperscript{19}. Equation (18) is one of those equations, and together with Eqs. (16) and (17) constitute a set which avoids obtaining the non-physical solutions that appear when solving the original set.

The critical point (where \( B = 0 \)) for \( \xi = 7.5 \), was located by solving numerically the set of Eqs. 16-18. We obtained \( K_c = 5.033605 \) and \( p_c = 0.46793635 \), for which \( B = 1.6 \times 10^{-16} \). These values are in agreement with those reported by Cummings and Stell\textsuperscript{22} for the same
value of $\zeta$. To obtain the critical exponent $\gamma$, we solved the set of equations at different values of $K (< K_c)$ along the critical isochore $\rho = \rho_c$. The results of such calculation are shown in Fig. 2 in which the coordinates are consistent with the definition of $\gamma$ given in Table I. The linear trend observed in this plot confirms that, as expected, $\gamma$ has the non-classical spherical model (SM) value of 2. The results obtained along the critical isotherm for densities in the neighborhood of the critical density $\rho_c$ are shown in Fig. 3. Again, the linear behavior observed for $\rho < \rho_c$ and for $\rho > \rho_c$ indicates that indeed $\delta = 5$. The slight deviation from linearity observed for the points which are closest to the critical point, is due to the fact that $B$ is not exactly zero at the critical point. These values of the critical exponents $\gamma$ and $\delta$ are in agreement with those obtained by Cummings and Stell\textsuperscript{22} who concluded, from algebraic manipulation of the analytical solution of MSA for the HCYF, that $\gamma = 2$ and $\delta = 5$.

4. NUMERICAL RESULTS

The finite-element approach, described in section 2, was used to generate solutions of MSA for the HCYF. As we mentioned before, the solution strategy was to progress by continuation from low density solution to higher density solutions. We also found in this case the rapid convergence obtained previously when solving other integral equations\textsuperscript{11,16,17} with the same numerical method. With the convergence criterion (Eq. (14)) $\Delta = 10^{-8}$, solutions were obtained in one to three iterations for steps in reduced density, $\rho$, as large as 0.1. Outside the critical region, the agreement between the values of the $c(r)$ obtained numerically and those obtained from the analytical solution is quite good. As the critical point is approached these values differ more importantly. Once a solution of MSA by the numerical method was found, the value of the isothermal bulk modulus $B = (\partial^2 \rho / \partial \rho)^T$ at a given $K = \epsilon / kT$ and $\rho$, were obtained from Eq. (6). The position of the critical point of the HCYF in the MSA with $\zeta = 7.5$ was determined with the following strategy: the isothermal bulk modulus was calculated along a supercritical isotherm with a value of $K$ not far
Fig. 2. The square root to the dimensionless isothermal bulk modulus divided by $K$, $(B/K)^{1/2}$, from Eqs. (16-18) along the critical isochore, $\rho = 0.46793635$, as a function of $K^{-1}$ for the HCYF with $\zeta = 7.5$ and $K < K_c$.
Fig. 3. The fourth root of the dimensionless isothermal bulk modulus times density, \((B\rho)^{\frac{1}{4}}\), from Eqs. (16-18) along the critical isotherm, \(K_c = 5.033605\), as a function of reduced density.
from the critical one. The density corresponding to the minimum of this curve was located, and a set of solutions with decreasing B was found on that isochore until a negative value of B was detected. Going back to the last point with a positive value of the isothermal bulk modulus, a new isotherm with that K was calculated and the process reinitiated. Further iterations of this procedure were used in order to refine the precision with which Kc and ρc were determined. The inverse critical temperature and critical density were found to be Kc' = 5.0400629 and ρc' = 0.46675, respectively. These values correspond to B = 2 × 10^-8 and agree with the analytical values Kc and ρc within 0.13% and 0.25%, respectively. For such calculation, a value of Δ = 10^-10 was used as the convergence criterion.

To determine the critical exponents γ we calculated several values of B for a set of values of K < Kc' along the critical isochore ρ = ρc', which we plotted in Fig. 4. The non-linear trend observed correspond to γ ≠ 2. Similarly, for the critical exponent δ, we plotted the results obtained numerically along the critical isotherm K = Kc (Fig. 5). Again, the non-linear behaviour exhibited corresponds to δ ≠ 5. These results are in clear disagreement with the analytical prediction. Finally, to calculate the values of γ and δ predicted by the numerical solution of MSA, we plotted ln(B/K) versus ln(K'/K - 1) and ln(Bp) versus ln |ρ/ρc' - 1| for ρ > ρc' and for ρ < ρc' as shown in Figures 6, 7 and 8, respectively. From the slopes of the lines fitted to the plots by a least squares criterion we obtained γ = 1.013 ± 0.002, δ(ρ > ρc') = 3.019 ± 0.006 and δ(ρ < ρc') = 2.963 ± 0.002, which are very close to the "classical" or mean field values (see Table 1).

5. DISCUSSION AND SUMMARY

The OZ relation plus a closure relation, such as PY, HNC or MSA yields a nonlinear integral equation of the second kind. The way to evaluate the nature of the approximations is to understand, as with any nonlinear equation, the nature of its solution space; that is, the function space augmented by parameters, boundary or asymptotic
Fig. 4. The square root of the dimensionless isothermal bulk modulus divided by \( K \), \((B/K)^{\frac{1}{2}}\), along the numerical critical isochore, \( \rho' = 0.46675 \), as a function of \( K^{-1} \). The dots represent the numerical solution of MSA for the HCYF with a cutoff \( R = 6\sigma \).
Fig. 5. The fourth root of the dimensionless isothermal bulk modulus times density, \((B\rho)_{4}\), along the numerical critical isotherm, \(K' = 5.0400629\), as a function of reduced density. As in Fig. 4 the dots represent the numerical solution of MSA for the HCYF with a cutoff \(R = 6\sigma\).
Fig. 6. Logarithmic plot of $B/K$ against $\tau = K'/K - 1$ along the numerical critical isochere. The dots correspond to the numerical solution of MSA for the HCYF with a cutoff $R = 6\sigma$. The line shown is a least squares fit of the data.
Fig. 7. Logarithmic plot of \( B \) against \( \nu^+ = \rho/\rho_c' - 1 \) along the numerical critical isotherm with \( \rho > \rho_c' \). The dots correspond to the finite element numerical solution if MSA for the HCYP with a cutoff \( R = 6\sigma \). The line shown is a least squares fit of the data.
Fig. 8. Logarithmic plot of $B_\rho$ against $\nu^- = 1 - \rho/\rho'_c$ along the numerical critical isotherm with $\rho < \rho'_c$. The dots correspond to the finite element numerical solution of MSA for the HCYF with a cutoff $R = 6\sigma$. The line shown is a least squares fit of the data.
conditions or other constraints.

The approach used here is modern numerical functional analysis\textsuperscript{25} and requires the aid of a powerful computer. It is well-suited to nonlinear integral equations for the following reasons:

a) matrix elements from the basis functions, that is, integrals like
\[ a_{ij} = \int_{0}^{R} \psi^i(r) \psi^j(r) \, dr , \]
are computed just once;

b) the local character of finite element basis functions makes disparate limiting behaviour easy to handle;

c) the efficiency of the method may be enhanced by adaptive element placement\textsuperscript{26};

d) coefficients of the basis functions represent local values of the unknown solution;

e) nonlinear functions and functionals are represented in terms of the linear basis\textsuperscript{27} leading to more efficient calculations;

f) Newton's method converges more rapidly than successive substitution (Picard iteration) and, near the solution, converges quadratically;

g) the converged Jacobian from Newton's method can be used to assess solution stability and sensitivity\textsuperscript{17}, to provide initial estimates of solutions for other conditions by continuation, and to obtain information about bifurcating solutions when they exist.

The finite element numerical method remained stable and efficient in obtaining solutions of MSA in the critical region. However, from the results shown in Sec. 4, it is clear that it fails to predict the
spherical model values for the critical exponents. The reason of this failure can be clarified if we express the dimensionless bulk modulus in terms of the total correlation function,

$$B = (1/kT) \left( \frac{\partial \rho / \partial \rho}{T} \right) = \left[ 1 + \rho \int h(r) dr \right]^{-1}. \quad (20)$$

The fact that the isothermal compressibility becomes infinite at the critical point can only be understood if the integral over $h(r)$ diverges for a system of infinite spatial extent. Consequently, the "long range" behaviour of $h(r)$ is essential in the correct determination of the thermodynamic properties in the critical neighborhood. The truncation of $h(r)$ for $r > R$ imposed in our numerical scheme limits the size of the density fluctuations, avoiding the divergence of the integral over $h(r)$ in Eq. (20) and makes the method unable to approach the critical point sufficiently closely. This result supports the conclusion obtained by Cummings and Monson$^{28}$ who, in a similar study using the Gillan method$^{29}$, showed that methods not dependent on an $r$-space truncation of $h(r)$ should be employed in the vicinity of liquid-gas critical points. In particular, for integral equations like MSA, which predict a large value of the critical exponents $\delta$, these methods must inevitably be used for a correct determination of this exponent. In this paper we have shown that numerical methods in which $h(r)$ is truncated at a finite value of $r$ not only fail to produce the correct values of the critical exponents, when they are nonclassical, but also tend to predict classical values for them. This may well have been the case for the numerical solution of MSA for the square-well fluid, for which "classical" critical exponents were obtained with the finite element method$^{30}$ for a cutoff $R = 7.5$.

It should be noted that, although the finite element method using the truncation of $h(r)$ at $r = R$ as asymptotic condition was, in the case presented, inadequate to give the correct values of the analytical exponents (at least for the small value of the truncation distance $R$ used), it allows to locate the critical point with a high accuracy for the value $\zeta = 7.5$ used in this work.
Studies like that of Cummings et al.\textsuperscript{28} and the one presented here show that considerable effort needs to be expended on the development of better numerical algorithms in order to analyze the critical behaviour predicted by integral equation approximations. At this point it must be remembered that the truncation of the total correlation function $h(r)$, as described above, is only the simplest asymptotic condition that can be imposed on $h(r)$. What remains to be done is to use a more appropriate asymptotic condition to account for the long tail of the correlation function in the neighborhood of the critical point, and see if the finite element numerical method is then able to predict the correct values of the critical exponents. For the HCYF in the MSA one fortunately has the analytical solution to compare with.

REFERENCES


8. See Ref. 1, p. 22.


