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A New Method for the Numerical Solution of Integral Equation Approximations[1]

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A new numerical technique for solving the Ornstein–Zernike equation is described. It is particularly useful in solving the Ornstein–Zernike equation for approximations and pair potentials (such as the Percus–Yevick and mean spherical approximations for finite ranged potentials) which imply a finite-ranged direct correlation function since for such approximations the numerical technique is essentially exact. The only approximation involved in such cases is the discretization of direct and total correlation functions over the finite range on which the direct correlation function is nonzero. Thus, the new method avoids truncation of the total correlation function and should permit the critical point and spinodal curve to be mapped out with greater accuracy than is permitted by existing methods. Preliminary explorations on the stability and accuracy of the method are described.

KEY WORDS: critical phenomena; integral equation approximations; numerical methods; Ornstein–Zernike equation.

1. INTRODUCTION

One of the aims of current research in liquid state physics is to develop a comprehensive (accurate both away and at critical points) statistical mechanical formalism which is applicable to model fluid systems interacting via quantitatively accurate intermolecular potentials. Aside from the intrinsic scientific interest in the successful development of such a for-

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malism, there are substantial practical benefits to be gained from such a theory of fluids. For example, the correlations typically employed in engineering design calculations [1] are based on equations of state which yield classical (or mean field) behavior at critical points (defined for liquid–gas critical points in technical detail in Table I) and consequently prove to be inaccurate in their vicinity. [In Table I, $\rho k_B T \chi_T \equiv k_B T(\partial \rho / \partial P)_T = 1 + \rho \int h(r)\, d\vec{r}$ and the quantities $\Delta\rho = \rho - \rho_c$, $\Delta T = T - T_c$. In these expressions, χ_T is the isothermal compressibility, ρ the number density, T the absolute temperature, k_B Boltzmann's constant, $h(r)$ the total correlation function (defined below), and ρ_c and T_c, respectively, the critical density and temperature.] At liquid–vapor critical points, the adverse effect of classical criticality is often seen most clearly in calculated densities, since according to experiment and modern theory, the density variation near the critical points of real systems is significantly stronger than that predicted classically.

Industrially important processes for which the behavior of fluid systems near their critical points becomes an issue include supercritical extraction [3] and enhanced (tertiary) oil recovery using CO_2 flooding where operating conditions often traverse mixture critical points [4]. Several *ad hoc* methods have been proposed which either attempt to incorporate results from renormalization group calculations into classical equations of state [5] or develop empirical correlations for specific properties such as the enthalpy of vaporization [6, 7]. However, rather than introducing the correct nonclassical critical behavior into the thermodynamic model in an empirical fashion, it would be more satisfactory approach to seek a consistent statistical mechanical basis from which thermodynamic models can be derived which treat fluid behavior correctly both at the critical point and in other regions of the phase diagram.

The predictions of integral equation approximations (IEAs) in the vicinity of the liquid–gas critical point have recently become the focus of renewed interest [8–25]. The reasons for this increased attention are that

Table I. Definition of the Major Critical Exponents for a Fluid in Three Dimensions in Terms of the Isothermal Compressibility χ_T

Exponent	Definition		MF[a]	SM[b]	Experiment [2]
γ	$\chi_T \sim (\Delta T)^{-\gamma}$,	$\rho = \rho_c,\ T \geqslant T_c$	1	2	1.24 ± 0.05
δ	$\chi_T \sim \lvert\Delta\rho\rvert^{1-\delta}$,	$T = T_c$	3	5	4.8 ± 0.2
η	$h(r) \sim r^{-1-\eta}$,	$\rho = \rho_c,\ T = T_c$	0	0	≈ 0.05

[a] Mean field (classical, Van der Waals) value.

[b] Spherical model value.

IEAs are exact through the first three virial coefficients of the pressure (and so are accurate at low density), are well characterized from a theoretical point of view through cluster expansions [26] (thus offering scope for systematic improvement), are acceptably accurate at dense gas and liquid state points, and are solved in orders of magnitude less time than corresponding, "exact" computer simulations. Consequently, at this point in time it appears that integral equations represent a promising route to a theory of molecular fluids with general applicability (i.e., both away from and in the vicinity of critical points).

The renewed interest in the predictions of fluid state IEA theories in the vicinity of the liquid–gas critical point of simple fluids was spurred by the work of Kozak, Luks, and collaborators on the solution of the Yvon–Born–Green equation (coupled with the Kirkwood superposition approximation, YBG-KSA) for the square well fluid in three dimensions [8, 9]. On the basis of numerical solution of this equation, Kozak, Luks, and collaborators analyzed the liquid–gas critical point of the square well fluid and reported that the YBG-KSA equation predicted nonclassical critical exponents (see Table I) in the range of experimentally determined values [9]. Subsequent analytic work [10], culminating in the papers of Fishman and Fisher [11], established that within the YBG-KSA equation there is in fact no critical point for the square well fluid in three dimensions. Kozak, Luks, and collaborators [12] have recently performed numerical studies which are consistent with Fishman's conclusions.

It is beyond the scope of this paper to review the many subsequent developments regarding the critical behavior of IEAs [13–25]. However, it should be pointed out that much of this work has focused on IEAs defined in terms of the Ornstein–Zernike (OZ)

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

in which $c(r)$ is the direct correlation function, $h(r)[=g(r)-1$, where $g(r)$ is the radial distribution function] is the total correlation function, and ρ is the number density. For example, the Percus–Yevick approximation [27] (PYA) for the exact independent, closure relation between $h(r)$ and $c(r)$ is given by

$$c(r) = f(r)[1 + h(r) - c(r)] \tag{2}$$

where $f(r) = \exp[-\phi(r)/k_B T] - 1$ is the Mayer f function, $\phi(r)$, k_B, and T are the intermolecular pair potential, Boltzmann's constant, and absolute temperature, respectively. For hard core systems $[\phi(r) = \infty, r < \sigma$, where σ

is the hard core diameter], the mean spherical approximation (MSA) is given by [26]

$$\begin{aligned} h(r) &= -1 \qquad & r<\sigma \\ c(r) &= -\phi(r)/k_B T \qquad & r>\sigma \end{aligned} \tag{3}$$

The hypernetted chain approximation (HNCA) is given by [26]

$$c(r) = f(r)\, y(r) + [y(r) - 1 - \ln y(r)] \tag{4}$$

where $y(r) = \exp[\phi(r)/k_B T]$ is known as the cavity distribution function. A summary of the present known status of these three IEAs is given in Table II.

As evidenced by the study by Kozak and co-workers and the present state of confusion regarding the HNCA, probing the critical phenomena of IEAs numerically poses several difficulties. As shown by Cummings and Monson [19, 20], who compared numerical solutions to IEAs with corresponding "exact" analytic solutions, the usual numerical methods employed to solve IEAs are able to approach the critical point accurately enough to determine γ and δ only if $\gamma \leqslant 2$ and $\delta \leqslant 3$. This is because larger values of these exponents require that $m = \rho k_B T/\chi_T \leqslant 10^{-4}$ at the critical point in order for the asymptotic behavior to be evident, a very difficult goal to achieve numerically.

In both studies [19, 20], the critical point was located numerically using Gillan's method [32], a highly efficient numerical technique for the solution of IEAs which combines Newton–Raphson and Picard iteration

Table II. Current Status of Knowledge Regarding the Critical Constants of the Three Main Integral Equation Approximations

Approximation	Critical behavior	Method	Reference(s)
PYA	MF[a]	Analytic	28, 13
	MF[a]	Numerical	15
	MF	Numerical/analytic	20
MSA	SM	Analytic	29
	SM	Numerical/analytic	19
HNCA	No true critical point	Numerical	30, 23
	Very small γ	Numerical	24
	No power law or logarithmic divergence in χ_T	Numerical	25

[a] With nonclassical scaling equation of state.

methods [33] in an insightful way. In common with most algorithms for the numerical solution of IEAs, Gillan's method requires the discretization of $h(r)$ and $c(r)$ into a set of N values representing $h(r_i)$ and $c(r_i)$, $r_i = i\Delta r$, $i = 1, \ldots, N$ and the assumption $h(r) = 0$ for $r \geqslant R = N\Delta r$. (A similar truncation is not always necessary for $c(r)$ since in the MSA, for example, its behavior for $r > \sigma$ is known analytically [19].) Thus the accuracy of any numerical scheme must be assessed as a function of Δr and R. Cummings and Monson [19] found that for larger R (and, to a lesser extent, smaller Δr) the calculated critical constants (density and temperature) come closer to their "exact" values (exact in this context meaning results obtained analytically).

Monson and Cummings [20] noted that, in both the MSA and PYA, the phase diagrams for the two fluids considered (the hard core Yukawa fluid [34] and AHSF, the adhesive hard sphere fluid [28]) can be divided into three regions: region I, in which analytically there are two real solutions, one of which is unphysical [$h(r)$ diverges at large r]; region II, in which analytically there are two real solutions, both of which diverge at large r (but one is the analytic continuation of the physically acceptable solution); and region III, in which there are two complex solutions which are complex conjugates. While acceptably accurate in region I, the usual Gillan method cannot yield correct results inside region II [because of the truncation of $h(r)$] or region III (because of the assumption of real solutions). One improvement that can be made to the Gillan method is to permit complex solutions as was done for the AHSF in the PYA by Monson and Cummings [20]. Inside region III, numerical solutions were found which have real and imaginary parts which are in good agreement with the analytic results [20]. This was the first numerical observation of complex solutions to an IEA.

2. NEW ALGORITHM FOR SOLVING INTEGRAL EQUATION APPROXIMATIONS

From the comparison between numerical and analytic solutions of IEAs [19, 20], it is clear that any numerical scheme which requires that $h(r) = 0$ for $r > R$ is unable to approach the critical point sufficiently closely either to enable the exponent δ to be determined unequivocably if it has a large enough value [19] or to predict the behavior of the total correlation function observed in region II. This suggests that a method not dependent on an r-space truncation of $h(r)$ should be employed in the vicinity of liquid–gas critical points. As well as the Gillan method and the usual Picard iteration, this rules out the finite-element method of Mier y Terán *et al.* [35].

One such algorithm was derived by Baxter [36] and used by Watts [30]. It is based on a factorization of the OZ equation and yields a numerical algorithm for the calculation of $h(r)$ under the sole assumption that $c(r)$ is finite ranged [i.e., $c(r)=0$ for $r>R$, as it is in the MSA and PY for finite-ranged potentials, and is effectively so for other potentials in these approximations]. Watts [37] also reported a private communication by Baxter which outlined an algorithm for employing the more celebrated Baxter factorization [38] in a numerical scheme. Baxter showed that if $c(r)=0$ for $r>R$ (i.e., the direct correlation function is finite-ranged, as it is in the PY and mean spherical approximations for finite-ranged potentials), then theOZ Eq. (1) can be written (factorized) into two equations:

$$rh(r) = -q'(r) + 2\pi\rho \int_0^R q(t)(r-t)\, h(|r-t|)\, dt \tag{5}$$

$$rc(r) = -q'(r) + 2\pi\rho \int_r^R q'(t)\, q(t-r)\, dt \tag{6}$$

The function $q(r)$ has the properties

$$q(r)=0 \qquad \text{for} \qquad r<0 \qquad \text{and} \qquad r \geqslant R \tag{7}$$

Baxter [38] suggested that the two equations (5) and (6) could be used, in conjunction with the closure relation, to iterate on the function $q(r)$, thus yielding a simple numerical method for solving the OZ equation. Several authors [31] used this concept to develop stable numerical for extending simulation data on radial distribution functions to large separations. In this paper, we introduce a variant of Baxter's idea which turns Eqs. (5) and (6) into an iterative scheme for the function $q'(r)$ as follows. We define $q_i' = q'(r_i)$, $H_i = r_i h(r_i)$, $C_i = r_i c(r_i)$ where, as before, $r_i = i\,\Delta r$, $i = 1, \ldots, N$, with $\Delta r = R/N$ being used in r-space to discretize the functions of interest. Suppose that $q_i'^{(n)}$, $q_i^{(n)}$, $H_i^{(n)}$, and $C_i^{(n)}$ are the nth iterates for the functions $q'(r)$, $rh(r)$, and $rc(r)$. We calculate $q_i^{(n)}$ from the formula

$$q_i^{(n)} = q_{i+1}^{(n)} - \frac{\Delta r}{2}\left[q_i'^{(n)} + q_{i+1}'^{(n)}\right], \qquad i = 1, \ldots, N-1 \tag{8}$$

which follows from using the trapezoidal rule to integrate $q'(r)$. From (7), we have $q_N'^{(n)} = 0$. From $q_i'^{(n)}$ and $q_i^{(n)}$, the $C_i^{(n)}$ are calculated using Eq. (6). The integration is performed using the trapezoidal rule, yielding

$$C_i^{(n)} = -q_i'^{(n)} + 2\pi\rho \sum_{p=i}^{N} \beta_p\, \Delta r\, q_i'^{(n)} q_{p-i}^{(n)} \tag{9}$$

where the β_p are the coefficients in the trapezoidal rule integration, $\beta_i = \beta_N = 1/2$, $\beta_p = 1$, $p = i+1, \ldots, N-1$. The nth iterate for $rh(r)$, $H_i^{(n)}$, is obtained from the closure relation. For example, the PY approximation yields

$$H_i^{(n)} = \exp[-\phi(r_i)/k_B T][H_i^{(n-1)} + r_i - C_i^{(n)}] - r_i \tag{10}$$

The penultimate step is to calculate $q_i'^{(\text{out})}$ from Eq. (5):

$$q_i'^{(\text{out})} = -H_i^{(n)} + 2\pi\rho \sum_{p=1}^{N} \zeta_p \operatorname{sgn}(i-p)\, H_{|i-p|}^{(n)} q_p^{(n)} \tag{11}$$

where $\operatorname{sgn}(x)$ is the sign function $[\operatorname{sgn}(x) = -1,\ x < 0,\ \operatorname{sgn}(x) = 1,\ x \geqslant 0]$ and $\zeta_1 = \zeta_N = 1/2$, $\zeta_p = 1$, $p = 2, \ldots, N-1$. The $(n+1)$st approximation for $q'(r)$ is then given by

$$q_i'^{(n+1)} = \alpha q_i'^{(\text{out})} + (1-\alpha)\, q_i'^{(n)} \tag{12}$$

where α is a mixing parameter designed to enhance convergence. Thus, our implementation of the Baxter idea amounts to an iteration on the function $q'(r)$, which we have found to be more reliable than iterating on $q(r)$ due to the inaccuracies that arise in numerical differentiation. Alternatively, one can recast the above equations into a set of nonlinear algebraic equations, the $q_i'^{(n)}$ which could then be solved using the Newton–Raphson technique. In this case, we can consider the numerical scheme above consist of solving the set of nonlinear equations

$$f_i(q_1'^{(n)}, \ldots, q_N'^{(n)}) \equiv q_i'^{(n)} - q_i'^{(\text{out})} = 0, \qquad i = 1, \ldots, N \tag{13}$$

since at the exact solution $q_i'^{(n)} - q_i'^{(\text{out})} = 0$. The Newton–Raphson technique requires that the Jacobian J, given by

$$J_{ij} = \frac{\partial f_i}{\partial q_j'^{(n)}} = \delta_{ij} - \frac{\partial q_i'^{(\text{out})}}{\partial q_j'^{(n)}} \tag{14}$$

be calculated. In Eq. (14), δ_{ij} is the Kronecker delta function. From Eqs. (8)–(12), it is straight-forward to evaluate $\partial q_i'^{(\text{out})}/\partial q_j'^{(n)}$ as follows:

$$\begin{aligned} \frac{\partial q_i'^{(\text{out})}}{\partial q_j'^{(n)}} = {} & -\frac{\partial H_i^{(n)}}{\partial q_j'^{(n)}} + 2\pi\rho\Delta r \left\{ \left[\frac{\partial q_1^{(n)}}{\partial q_j'^{(n)}} H_i^{(n)} + q_1^{(n)} \frac{\partial H_i^{(n)}}{\partial q_j'^{(n)}} \right] \right. \\ & \left. + \sum_{p=1}^{N-1} \left[\frac{\partial q_p^{(n)}}{\partial q_j'^{(n)}} \operatorname{sgn}(i-p)\, H_{i-p}^{(n)} + q_p^{(n)} \operatorname{sgn}(i-p) \frac{\partial H_{i-p}^{(n)}}{\partial q_j'^{(n)}} \right] \right\} \end{aligned} \tag{15}$$

where

$$\frac{\partial H_i^{(n)}}{\partial q_j^{\prime(n)}} = -\exp[-\phi(r_i)/k_{\mathrm{B}}T]\,\frac{\partial C_i^{(n)}}{\partial q_j^{\prime(n)}} \tag{16}$$

$$\frac{\partial C_i^{(n)}}{\partial q_j^{\prime(n)}} = -\delta_{ij} + 2\pi\rho\Delta r\left[\frac{1}{2}\left(\delta_{ij}q_1^{(n)} + q_i^{\prime(n)}\frac{\partial q_1^{(n)}}{\partial q_j^{\prime(n)}} + \delta_{Nj}q_{N-i}^{(n)} + q_N^{\prime(n)}\frac{\partial q_{N-i}^{(n)}}{\partial q_j^{\prime(n)}}\right)\right.$$
$$\left. + \sum_{p=i+1}^{N}\left(\delta_{pj}q_{j-i}^{(n)} + q_p^{\prime(n)}\frac{\partial q_{p-i}^{(n)}}{\partial q_j^{\prime(n)}}\right)\right] \tag{17}$$

$$\frac{\partial q_i^{(n)}}{\partial q_j^{\prime(n)}} = -\frac{\Delta r}{2}(\delta_{ij} + \delta_{Nj}) - \Delta r\sum_{p=i+1}^{N-1}\delta_{pj}, \qquad i = 1,\ldots, N-1 \tag{18}$$

From 7, $\partial q_N^{(n)}/\partial q_j^{\prime(n)} = 0$.

Thus far, a preliminary evaluation of the proposed algorithm has been made for the PYA applied to the square well fluid with pair potential

$$\begin{aligned} \phi_{\mathrm{SW}}(r) &= \infty, && r < \sigma \\ &= -\varepsilon, && \sigma < r < R \\ &= 0, && r > R \end{aligned} \tag{19}$$

with $R = 1.5\sigma$. The square well fluid yields a $q'(r)$ which is discontinuous at $r = \sigma$. To contrast with the square well fluid, the PYA for a shifted Lennard–Jones potential given by

$$\begin{aligned} \phi_{\mathrm{SLJ}}(r) &= \phi_{\mathrm{LJ}}(r) - \phi_{LJ}(R_c), && r < R_c \\ &= 0, && r > R_c \end{aligned} \tag{20}$$

where $\phi_{\mathrm{LJ}}(r)$ is given by

$$\phi_{\mathrm{LJ}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

was also considered because in this case $q'(r)$ is continuous. Since at zero density, $q'(r) = -rf(r)$, one can find the solution for $q'(r)$ along an isotherm beginning at low density using this formula as a convenient initial guess.

From our explorations to date, the following conclusions can be drawn.

(1) For straightforward iteration to be successful, a reasonably large number of points N, such as $N \approx 300$, must be used. This is true for both the square well and the shifted Lennard–Jones potential

and, therefore, does not appear to be a consequence of discontinuities in $q'(r)$.

(2) When convergent, the method gives results that are in agreement with other calculations. This is exemplified in Fig. 1, where for $\varepsilon/k_B T = 0.5$ and $\rho\sigma^3 = 0.5$, we compare the results of the Gillan method and the Baxter method for the PYA applied to the square well fluid. The solid curve is obtained using the method based on Baxter's factorization described in above with $N = 300$ and $R = 1.5\sigma$. The dashed curve is obtained using Gillan's method, with 256 points evenly spaced over the domain $(0, 6.4\sigma)$. The advantage of the Baxter method is that functions $h(r)$, $c(r)$, and $q'(r)$ are required only on the interval $0 < r < R$, and as a consequence, a very fine grid for these functions is attainable.

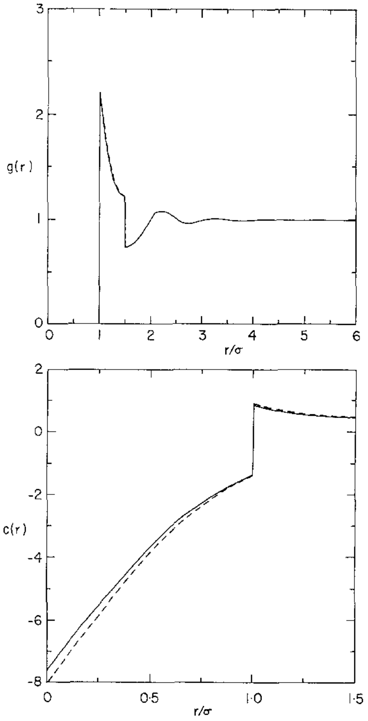

Fig. 1. The radial distribution function and direct correlation function for the square well fluid [see Eq. (19)] at $\varepsilon/k_B T = 0.5$ and $\rho\sigma^3 = 0.5$ and with cutoff $R = 1.5\sigma$. Solid curve, algorithm described in text; dashed curve, Gillan method.

Consequently, the density of points in the r-space discretization for the factorization-based method is 10 times that of the Gillan result.

(3) Applying the Newton–Raphson (NR) algorithm as described above is computationally intensive for $N > O(10^2)$ and our explorations were limited to the square well fluid with $N = 60$ points. It was found that the NR method was not stable if the initial guess was some distance from the final solution. The best results were obtained by using the iteration scheme to get close to the final solution and then applying one or two NR cycles to accelerate convergence over the last few iterates.

(4) Using iteration alone, one can obtain results for isotherms with $\varepsilon/k_B T \leqslant 0.7$ without difficulty. Convergence problems are encountered along lower temperature isotherms, although it is possible by parametric continuation in $\varepsilon/k_B T$ at fixed density to obtain solutions at lower temperatures (such as $\varepsilon/k_B T = 1.0$).

3. CONCLUSIONS

The results obtained to date with the factorization-based numerical scheme have been mixed and indicate that considerably more work needs to be done if the algorithm is to be useful for its intended purpose (i.e., to permit the exploration of the near-critical and two-phase regions of the phase diagram). The results suggest that a combination of iteration and NR steps is the most effective overall strategy for numerical stability. However, it is clearly numerically costly to use as many points in the NR step as are required in the iteration step. Thus, a method of combining the two steps requires mapping the iteration points onto a smaller number of points which are refined by the NR step. This is, in fact, the Gillan philosophy [32]. Its application to the present algorithm is the current focus of our ongoing research efforts.

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