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An Efficient Gauss–Newton-like Method for the Numerical Solution of the Ornstein–Zernike Integral Equation for a Class of Fluid Models*

STANISLAV LABÍK, ROMAN POSPÍŠIL, AND ANATOL MALIJEVSKÝ

Department of Physical Chemistry, Institute of Chemical Technology, Prague 166 28, Czech Republic

AND

WILLIAM ROBERT SMITH

Department of Mathematics and Statistics, University of Guelph, Guelph, Ontario N1G 2W1, Canada

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A numerical algorithm for solving the Ornstein–Zernike (OZ) integral equation of statistical mechanics is described for the class of fluids composed of molecules with axially symmetric interactions. Since the OZ equation is a nonlinear second-kind Fredholm equation whose key feature for the class of problems of interest is the highly computationally intensive nature of the kernel, the general approach employed in this paper is thus potentially useful for similar problems with this characteristic. The algorithm achieves a high degree of computational efficiency by combining iterative linearization of the most complex portion of the kernel with a combination of Newton–Raphson and Picard iteration methods for the resulting approximate equation. This approach makes the algorithm analogous to the approach of the classical Gauss–Newton method for nonlinear regression, and we call our method the GN algorithm. An example calculation is given illustrating the use of the algorithm for the hard prolate ellipsoid fluid and its results are compared directly with those of the Picard iteration method. The GN algorithm is four to ten times as fast as the Picard method, and we present evidence that it is the most efficient general method currently available.

1. INTRODUCTION

The Ornstein–Zernike (OZ) equation is a nonlinear Fredholm second-kind integral equation employed in the statistical mechanics of fluids to compute their microscopic structure from a description of the underlying intermolecular forces. The principal structural quantity of interest is the pair correlation function, $g(12)$, which is proportional to the probability of observing a pair of molecules 1 and 2 at given relative distance and mutual orientation. Theories based on the OZ equation for $g(12)$, and on closures such as the Percus–Yevick (PY) and hypernetted chain (HNC) provide a standard route to the structure of fluids [1].

In the case of simple fluids (those with spherically symmetric intermolecular potentials) the equation involves a one-dimensional integral, whereas for molecular fluids (those for which the intermolecular potential depends on relative orientation in addition to distance) the integral is in general five-dimensional. Solving the OZ equation for molecular fluids is thus much more difficult than for simple fluids. For most systems and closures the equation must be solved numerically, typically following discretization and conversion to a set of nonlinear transcendental equations.

For the discretized OZ equation, the full Newton–Raphson (NR) method, although possessing good convergence properties, is usually unsuitable due to the large numbers of unknowns involved, and the most often-used method of solution has been the Picard iteration method in configuration space [2] or in Fourier space (PF) [3].Picard iteration has the disadvantages that convergence is typically slow, uncertain, and sensitive to the initial estimate. For simple fluids (for which $g(12) \equiv g(r_{12})$), more powerful numerical procedures have been developed, which remove the inherent convergence problems of Picard iteration [4–10].

Only for the simplest molecular fluids, those composed of axially symmetric (linear) molecules (for which $g(12)$ depends on one distance and three angular variables), have general numerical methods of solution of the OZ equation been developed. The first such method was proposed by Lado [11], based on the earlier work of Blum [12] and of Chen and Steele [13]. It consists of expanding the correlation functions in spherical harmonics, writing the OZ equation as a set of nonlinear equations in Fourier space, and solving these by the PF method. A similar procedure, also based on the spherical harmonic expansion and the PF method, was proposed by Fries and Patey [14, 15]. An improvement to this algorithm has been recently described

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by Kinoshita and Harada [16], which partially incorporates the NR method in a manner similar to that proposed by Gillan for simple fluids [5]. Finally, an approximate method based on interpolation of the pair distribution function at a small number of specific orientations has been proposed by Lago and Sevilla [17], who employed Picard iteration in configuration space. All these approaches are very computationally intensive.

The purpose of this paper is to describe the details of an efficient numerical algorithm for solving the OZ equation in conjunction with an arbitrary closure relation for linear molecular fluids. The algorithm is a generalization of that proposed for simple fluids by two of the present authors [6]. Due to its relationship to an approach used in nonlinear regression problems, we call our algorithm the GN (for Gauss–Newton) method. We have recently used this algorithm to study several OZ closures for a number of different molecular fluids, including hard homonuclear [18, 19] and heteronuclear [20] diatomics, hard triatomics [21], hard prolate [22] and oblate spherocylinders [23], hard prolate ellipsoids of revolution [24], Lennard-Jones diatomics [25], and hard quadrupolar diatomics [26]. We believe that the approach of the GN method is capable of being used in the context of the numerical solution of other nonlinear integral equations.

In the next section, we consider the basic relations involving the Ornstein–Zernike equation and the correlation functions in the case of linear molecules. In the following section, we discuss the main steps involved in implementing the PF method and focus on the most time-consuming steps in the case of molecular fluids. The next section describes the GN algorithm, which seeks to decrease the computation time involved in these steps, as well as to improve its convergence properties. The final section presents a numerical example of an implementation of the GN method and directly compares it with an implementation of the PF method of Lado [11]. Finally, we compare the GN algorithm with other available methods and discuss possible modifications and extensions of our approach.

2. THE OZ EQUATION FOR LINEAR MOLECULAR FLUIDS

The OZ equation in Fourier space is given by

$$\tilde{\gamma}(12) = \frac{\rho}{\Omega} \int \tilde{c}(13)[\tilde{c}(32) + \tilde{\gamma}(32)]\, d\boldsymbol{\omega}_3, \tag{1}$$

where $\Omega = \int d\boldsymbol{\omega}_3$ and ρ is the number density. Tilde's denote Fourier transforms of the direct correlation function, $c(12)$, and the series function $\gamma(12) = h(12) - c(12)$, where $h(12) = g(12) - 1$ is the total correlation function. For linear molecules, $\Omega = 4\pi$, and the pair correlation functions $X(12)$ may be expressed as

$$X(12) \equiv X(r, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2) = X(r, \theta_1, \theta_2, \phi_{12}), \tag{2}$$

where $r \equiv r_{12}$ is the distance between respective reference points in molecules 1 and 2, $\boldsymbol{\omega}_i = (\theta_i, \phi_i)$ is the vector of angles defining the orientation of the molecular axis of molecule i with respect to the axis joining the reference points, and $\phi_{12} = \phi_1 - \phi_2$. The OZ equation must be coupled with a closure, which may be written in general as

$$c(12) = \exp[-\beta u(12) + \gamma(12) - B(12)] - 1 - \gamma(12), \tag{3}$$

where $\beta = 1/kT$, $u(12)$ is the intermolecular pair potential, and $B(12)$ is the bridge function, the particular form of which implements the closure.

The correlation functions $X(12)$ may be expanded in normalized spherical harmonics,

$$X(12) = 4\pi \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \sum_{m=-n}^{n} X_{l_1 l_2 m}(r) \times Y_{l_1 m}(\theta_1, \phi_1)\, Y_{l_2, \bar{m}}(\theta_2, \phi_2), \tag{4}$$

where $n = \min(l_1, l_2)$, and $\bar{m} = -m$. The harmonic coefficients are given by

$$X_{l_1 l_2 m}(r) = \tfrac{1}{2} \int_{-1}^{1} \int_{-1}^{1} \int_{-\pi}^{\pi} d\cos\theta_1\, d\cos\theta_2\, d\phi_{12} \times X(12)\, Y_{l_1 \bar{m}}(\theta_1, \phi_1)\, Y_{l_2 m}(\theta_2, \phi_2). \tag{5}$$

The Fourier transforms, $\tilde{X}(12)$, of the correlation functions may be also expanded in spherical harmonics,

$$\tilde{X}(12) = 4\pi \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \sum_{m=-n}^{n} \tilde{X}_{l_1 l_2 m}(k) \times Y_{l_1 m}(\theta'_1, \phi'_1)\, Y_{l_2 \bar{m}}(\theta'_2, \phi'_2), \tag{6}$$

where $k \equiv k_{12}$. The OZ equation (1) may be written in terms of the harmonic coefficients of $\tilde{c}$ and $\tilde{\gamma}$,

$$\tilde{\gamma}_{l_1 l_2 m}(k) = (-)^m \rho \sum_{l_3=m}^{\infty} \tilde{c}_{l_1 l_3 m}(k) \times [\tilde{c}_{l_3 l_2 m}(k) + \tilde{\gamma}_{l_3 l_2 m}(k)]. \tag{7}$$

Finally, it is convenient to use the correlation functions $C(12) \equiv rc(12)$, $\tilde{C}(12) \equiv k\tilde{c}(12)$, $\Gamma(12) \equiv r\gamma(12)$, and $\tilde{\Gamma}(12) \equiv k\tilde{\gamma}(12)$. Equations (3) and (7) then become, respectively,

$$C(12) = r \exp[-\beta u(12) + \Gamma(12)/r - B(12)] - r - \Gamma(12) \tag{8}$$

and

$$\tilde{\Gamma}_{l_1 l_2 m}(k) = \frac{(-)^m \rho}{k} \sum_{l_3=m}^{\infty} \tilde{C}_{l_1 l_3 m}(k) \times [\tilde{C}_{l_3 l_2 m}(k) + \tilde{\Gamma}_{l_3 l_2 m}(k)]. \tag{9}$$

3. PICARD ITERATION FOR SIMPLE AND MOLECULAR FLUIDS

In this section we summarize the Lado version of the PF method [11] with some minor modifications, in order to motivate the GN algorithm.

The variables r and k are discretized at values $r_i = i\,\Delta r$, $k_j = j\,\Delta k$; $i, j = 1, ..., N$, where $\Delta r\,\Delta k = \pi/N$ for some appropriate choice of mesh sizes Δr, Δk, and truncation limit N. Similarly, the harmonic coefficient indices are truncated at limits L_1, L_2, M. In a typical case considered later in this paper, $N = 1024$, $\Delta r = 0.01$, $L_1 = L_2 = 6$, $M = 4$. The OZ equation (9) with the closure (8) then becomes a set of nonlinear transcendental equations in the values of the unknown harmonic coefficients in real and Fourier space at the grid points $\{r_i, k_j\}$.

The PF method starts from an initial estimate of $\tilde{\Gamma}_{l_1 l_2 m}(k_j)$ and each iteration consists of the following four steps:

(i) *Transformation to configuration space*, $\tilde{\Gamma}_{l_1 l_2 m}(k_j) \to \Gamma_{l_1 l_2 m}(r_i)$. First, the harmonic coefficients $\tilde{\Gamma}_{l_1 l_2 m}(k_j)$ in the intermolecular coordinate frame are transformed to harmonic coefficients $\tilde{\Gamma}(k_j; l_1 l_2 l)$ in the space-fixed coordinate frame. Then inverse Hankel (Fourier–Bessel) transformation is performed to obtain $\Gamma(r_i; l_1 l_2 l)$. These are then transformed to the coefficients $\Gamma_{l_1 l_2 m}(r_i)$ in the intermolecular coordinate frame. The procedure is described in detail in Ref. [11].

(ii) *Closure*, $\Gamma_{l_1 l_2 m}(r_i) \to C_{l_1 l_2 m}(r_i)$. The harmonic coefficients $C_{l_1 l_2 m}(r_i)$ of $C(12)$ are calculated from $\Gamma_{l_1 l_2 m}(r_i)$ using the closure equation (8),

$$\begin{aligned} C_{l_1 l_2 m}(r_i) = {} & \tfrac{1}{2} \int_{-1}^{1} \int_{-1}^{1} \int_{-\pi}^{\pi} d\cos\theta_1\, d\cos\theta_2\, d\phi_{12} \\ & \times Y_{l_1 \bar{m}}(\theta_1, \phi_1)\, Y_{l_2 m}(\theta_2, \phi_2) \\ & \times \{r_i \exp[-\beta u(12) + \Gamma(12)/r_i - B(12)] \\ & - r_i - \Gamma(12)\}, \end{aligned} \tag{10}$$

where $\Gamma(12)$ is obtained from $\Gamma_{l_1 l_2 m}(r_i)$, using the spherical harmonic expansion (4).

(iii) *Transformation to Fourier space*, $C_{l_1 l_2 m}(r_i) \to \tilde{C}_{l_1 l_2 m}(k_j)$. The harmonic coefficients $C_{l_1 l_2 m}(r_i)$ are transformed to the coefficients $\tilde{C}_{l_1 l_2 m}(k_j)$. The procedure is analogous to that of step (i).

(iv) *Use of the OZ equation*, $\tilde{C}_{l_1 l_2 m}(k_j) \to \tilde{\Gamma}_{l_1 l_2 m}(k_j)$. The set of linear equations (9) is solved for the $\tilde{\Gamma}_{l_1 l_2 m}(k_j)$.

The final results $\tilde{\Gamma}$ of step (iv) above are taken as the initial estimate for the next iteration in step (i).

We remark that, in practice, a relaxation parameter $\lambda \in (0, 1)$ is sometimes also incorporated to improve convergence in difficult cases, by means of which the estimate on the next iteration is taken to be the initial estimate plus a factor λ of the difference between the final and initial results of the basic Picard iteration step described above. Since such a procedure may be incorporated into *any* numerical algorithm (including the one described in this paper), we do not consider it to be a distinguishing feature of the basic algorithm itself. We briefly mention the use of relaxation parameters in the discussion at the end of the paper.

The PF method of solution described above is formally identical to the PF method used for simple fluids, with the only formal difference being the absence of spherical harmonic expansions in the latter case. However, the relative computation times required for each of the steps in a single PF iteration differ considerably for the two types of fluids. For simple fluids, the most time-consuming steps are (i) and (iii), the calculation of the Fourier transforms, while steps (ii) and (iv) are computationally trivial. For molecular fluids, the computation of Hankel transforms in steps (i) and (iii) (including recalculations between coordinate frames), while more complex than the calculation of Fourier transforms in the case of simple fluids, consumes only a small fraction of the total computation time per iteration. Similarly, step (iv) does not greatly add to the complexity of the calculation in the case of molecular fluids. Step (ii) is by far the most time-consuming, since it involves calculations of the three-dimensional integrals in (10) for ~1000 intermolecular distances r_i and for more than 20 harmonic coefficients. Thus, a prime candidate for improving the efficiency of the PF algorithm in the case of molecular fluids is to reduce the number of times that step (ii) must be performed.

In addition, we emphasize that a known general deficiency of the PF method is its inherently poor convergence. It requires a good initial estimate and convergence is generally slow and/or uncertain. For example, it is not unusual for the PF method to require ~100 iterations at high densities and to be divergent at some state points, even for a very good initial estimate and use of relaxation parameters (e.g., [15, 16]). This, of course, is also the case for simple fluids, but it is much more crucial for molecular fluids, due to the greater complexity of the calculations involved.

4. THE GN ALGORITHM

Equation (9) must be solved numerically at a set of discretized values k_j. Use of the full NR method on the resulting set of nonlinear algebraic equations would provide rapid convergence, but this is impractical due to the large numbers of variables involved. For example, 28 harmonic coefficients and ~ 1000 values of k_j would result in a set of ~ 28000 linear equations, with millions of elements in the coefficient matrix.

Our algorithm is motivated by the fact that each iteration of the full NR procedure applied to (9) involves two separate linearizations, followed by the numerical solution of the resulting set of linear equations. Equation (9) may be written symbolically as

$$\tilde{\mathbf{\Gamma}} = \tilde{\mathbf{f}}[\tilde{\mathbf{C}}(\tilde{\mathbf{\Gamma}}), \tilde{\mathbf{\Gamma}}]. \tag{11}$$

Each iteration of the full NR method involves linearizing both the "inner" nonlinearity $\tilde{\mathbf{C}}(\tilde{\mathbf{\Gamma}})$ and the "outer" nonlinearity $\mathbf{f}$. The inner nonlinearity involves the closure relation and the outer nonlinearity involves the OZ equation itself. Our algorithm focuses on the inner linearization. As a consequence, it may thus be considered to be in the same spirit as the Gauss–Newton method for nonlinear regression [27], and we accordingly call it the GN algorithm.

Each iteration of the GN algorithm consists of two separate stages. The first stage involves linearization of the closure relation (8). When substituted into (9), this results in a modified OZ equation, which we call the linearized-closure Ornstein–Zernike (LC–OZ) equation. This linearization step is the essential feature of the method, and it will be shown that use of this equation results in a considerable time saving as compared with use of the OZ equation using the full closure (10), as in step (ii) of the PF method. The second stage involves discretizing and numerically solving the LC–OZ equation. Although this can be implemented in a number of ways, we describe here an efficient procedure based on a combination of NR and Picard iteration.

4.1. *Linearization of the Closure and the LC–OZ Equation*

We denote initial estimates by the superscript *in*. The closure relation (8), expanded to first order about the initial estimate gives

$$C(12) = C^{in}(12) + \phi^{in}(12)[\Gamma(12) - \Gamma^{in}(12)], \tag{12}$$

where

$$\begin{aligned}\phi^{in}(12) &= \left(\frac{\partial C(12)}{\partial \Gamma(12)}\right)_{\Gamma^{in}} \\ &= [C^{in}(12) + \Gamma^{in}(12)]/r - \left(\frac{\partial B(12)}{\partial \Gamma(12)}\right)_{\Gamma^{in}} \\ &\quad \times [C^{in}(12) + \Gamma^{in}(12) + r].\end{aligned} \tag{13}$$

The derivative $\phi^{in}(12)$ depends on the chosen theory, i.e., on the approximation used for $B(12)$. For example, the PY closure ($B(12) = \Gamma(12)/r - \ln[1 + \Gamma(12)/r]$) gives

$$\phi^{in}(12) = \exp[-\beta u(12)] - 1.$$

In the case of closures for which $B(12)$ does not depend on $\Gamma(12)$, such as the HNC, reference HNC [28] and NSB [18] closures, the last term in (13) vanishes.

The linearization (12) allows $C_{l_1 l_2 m}(r)$ to be obtained by means of Parseval's theorem [29],

$$\begin{aligned}C_{l_1 l_2 m}(r) &\\ = C^{in}_{l_1 l_2 m}(r) &\\ + \sum_{l_1'' l_2'' m''} \sum_{l_1' l_2' m'} &\left[\frac{(2l_1'+1)(2l_1''+1)(2l_2'+1)(2l_2''+1)}{(2l_1+1)(2l_2+1)}\right]^{1/2} \\ &\times C(l_1' l_1'' l_1; m'm''m)\, C(l_2' l_2'' l_2; 000) \\ &\times C(l_2' l_2'' l_2 : \bar{m}'\bar{m}''\bar{m})\, C(l_2' l_2'' l_2; 000) \\ &\times \phi^{in}_{l_1' l_2' m'}(r)[\Gamma_{l_1'' l_2'' m''}(r) - \Gamma^{in}_{l_1'' l_2'' m''}(r)],\end{aligned} \tag{14}$$

which may be written symbolically as

$$\begin{aligned}C^*_{l_1 l_2 m}(r) = C^{in}_{l_1 l_2 m}(r) + \sum_{l_1'' l_2'' m''} &\alpha^{in}(l_1, l_2, m; l_1'' l_2'' m''; r) \\ &\times [\Gamma^*_{l_1'' l_2'' m''}(r) - \Gamma^{in}_{l_1'' l_2'' m''}(r)],\end{aligned} \tag{15}$$

where superscript * is used to denote the linearized quantities. The summations are performed over l_1', l_1'', l_2', m', m'' for all nonvanishing Clebsch–Gordan coefficients $C(ijk; lmn)$.

Substituting (15) in the OZ equation (9) gives an equation for the corresponding linearized harmonics $\tilde{\Gamma}^*$,

$$\begin{aligned}\tilde{\Gamma}^*_{l_1 l_2 m}(k) = \frac{(-)^m \rho}{k} \sum_{l_3 = m}^{\infty} &\tilde{C}^*_{l_1 l_3 m}(k) \\ &\times [\tilde{C}^*_{l_3 l_2 m}(k) + \tilde{\Gamma}^*_{l_3 l_2 m}(k)],\end{aligned} \tag{16}$$

which we call the LC–OZ equation. Each main iteration of the GN algorithm involves the solution of the LC–OZ equation (16) for $\tilde{\Gamma}^*_{l_1 l_2 m}(k)$ at a set of discretized values $\{k_j = j\,\Delta k,\ j = 1, \ldots, N\}$, using (15). Use of the linearized closure (15) instead of the full closure (10) makes (16) much easier to solve than the full OZ equation (9).

The GN method proceeds from an initial estimate $\tilde{\Gamma}^{in}$, and $C^{in}(12)$ and $\phi^{in}(12)$ are then calculated from (10) and (13), respectively. The coefficients α in (15) are determined from (14), and (15) is substituted into the LC–OZ equation (16), which is solved by the method described in the next section. The resulting solution $\tilde{\Gamma}^*$ is used as the next estimate, $\tilde{\Gamma}^{in}$, and the procedure is repeated until numerical convergence is achieved.

4.2. *Efficient Solution of the LC–OZ Equation*

The GN method consists of the iterative solution of the LC–OZ equation (16), which is a set of coupled quadratic equations in $\tilde{\Gamma}^*_{l_1 l_2 m}(k_j)$. A particular implementation of the method requires the use of a numerical algorithm to solve this equation. The overall behaviour of the GN methods depends critically on the efficiency of the method chosen.

When discretized at a set of values k_j, application of the full NR method to the LC–OZ equation remains impractical. The method proposed previously for simple fluids [6], using a combination of NR and Picard iteration, was shown to be very efficient. Here we follow a similar approach. We describe the procedure for correlation functions in the centre–centre molecular coordinate frame. The relevant formulae in the site–site coordinate frame are given in Appendix B.

Each iteration for solving the LC–OZ equation consists of two separate steps. First, the full NR method is used for the most important (primary) solution components, which we take to be the first J values of the two leading harmonic coefficients, $\tilde{\Gamma}^*_{000}(k_j)$ and $\tilde{\Gamma}^*_{200}(k_j)$, $j \leqslant J$. The unknowns $\tilde{\Gamma}^*_{000}(k_j)$, $\tilde{\Gamma}^*_{200}(k_j)$, $j > J$, and the higher harmonic coefficients $\tilde{\Gamma}^*_{l_1 l_2 m}(k_j)$ are kept constant during this stage. Following convergence of this procedure, the second step consists of a single Picard iteration on (16) to adjust the remaining (secondary) harmonic coefficients, using values of the primary $2J$ unknowns obtained from the NR step. This two-step iteration is then repeated until convergence is achieved for the entire LC–OZ equation (16). By means of this technique, we only use the full NR method on the LC–OZ equation for the most critical $2J$ solution components, and we use Picard iteration for the less critical harmonics. This avoids the construction and solution of the large sets of linear equations that would be required to implement the full NR method for all the harmonics, while retaining some of its desirable convergence characteristics.

The details of the first (NR) steps are as follows. The LC–OZ equation (16) for the first J values of $\tilde{\Gamma}^*_{000}(k_j)$ and $\tilde{\Gamma}^*_{200}(k_j)$ may be written

$$\begin{aligned}
F_0(k_j) = {} & -\tilde{\Gamma}^*_{000}(k_j) + \frac{\rho}{k_j}\Big\{\tilde{C}^*_{000}(k_j)[\tilde{C}^*_{000}(k_j) + \tilde{\Gamma}^*_{000}(k_j)] \\
& + \tilde{C}^*_{200}(k_j)[\tilde{C}^*_{200}(k_j) + \tilde{\Gamma}^*_{200}(k_j)] \\
& + \sum_{l_3=4}^{\infty} \tilde{C}^*_{l_3 00}(k_j)[\tilde{C}^*_{l_3 00}(k_j) + \tilde{\Gamma}^*_{l_3 00}(k_j)]\Big\} \\
= {} & 0, \qquad j = 1, 2, \ldots, J, \\
F_1(k_j) = {} & -\tilde{\Gamma}^*_{200}(k_j) + \frac{\rho}{k_j}\Big\{\tilde{C}^*_{200}(k_j)[\tilde{C}^*_{000}(k_j) + \tilde{\Gamma}^*_{000}(k_j)] \\
& + \tilde{C}^*_{220}(k_j)[\tilde{C}^*_{200}(k_j) + \tilde{\Gamma}^*_{200}(k_j)] \\
& + \sum_{l_3=4}^{\infty} \tilde{C}^*_{l_3 20}(k_j)[\tilde{C}^*_{l_3 00}(k_j) + \tilde{\Gamma}^*_{l_3 00}(k_j)]\Big\} \\
= {} & 0, \qquad j = 1, 2, \ldots, J.
\end{aligned} \tag{17}$$

Using a superscript 0 to denote evaluation at an initial estimate and keeping the final summations in (17) fixed, the NR equations resulting from (17) are

$$\begin{aligned}
& F^0_0(k_j) + \sum_{m=1}^{J}\left(\frac{\partial F_0(k_j)}{\partial \tilde{\Gamma}^*_{000}(k_m)}\right)_{\tilde{\Gamma}^0}[\tilde{\Gamma}^*_{000}(k_m) - \tilde{\Gamma}^0_{000}(k_m)] \\
& \quad + \sum_{m=1}^{M}\left(\frac{\partial F_0(k_j)}{\partial \tilde{\Gamma}^*_{200}(k_m)}\right)_{\tilde{\Gamma}^0}[\tilde{\Gamma}^*_{200}(k_m) - \tilde{\Gamma}^0_{200}(k_m)] \\
& = 0, \qquad j = 1, 2, \ldots, J, \\
& F^0_1(k_j) + \sum_{m=1}^{J}\left(\frac{\partial F_1(k_j)}{\partial \tilde{\Gamma}^*_{000}(k_m)}\right)_{\tilde{\Gamma}^0}[\tilde{\Gamma}^*_{000}(k_m) - \tilde{\Gamma}^0_{000}(k_m)] \\
& \quad + \sum_{m=1}^{J}\left(\frac{\partial F_1(k_j)}{\partial \tilde{\Gamma}^*_{200}(k_m)}\right)_{\tilde{\Gamma}^0}[\tilde{\Gamma}^*_{200}(k_m) - \tilde{\Gamma}^0_{200}(k_m)] \\
& = 0, \qquad j = 1, 2, \ldots, J,
\end{aligned} \tag{18}$$

where the elements of the Jacobian matrix are obtained from (17) as

$$\begin{aligned}
& \left(\frac{\partial F_0(k_j)}{\partial \tilde{\Gamma}^*_{000}(k_m)}\right)_{\tilde{\Gamma}^0} \\
& \quad = \delta_{jm}\left[-1 + \frac{\rho}{k_j}\tilde{C}^0_{000}(k_j)\right] \\
& \qquad + \frac{\rho}{k_j}[2\tilde{C}^0_{000}(k_j) + \tilde{\Gamma}^0_{000}(k_j)]\left(\frac{\partial \tilde{C}_{000}(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\tilde{\Gamma}^{\mathrm{in}}} \\
& \qquad + \frac{\rho}{k_j}[2\tilde{C}^0_{200}(k_j) + \tilde{\Gamma}^0_{200}(k_j)]\left(\frac{\partial \tilde{C}_{200}(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\tilde{\Gamma}^{\mathrm{in}}}, \\
& \left(\frac{\partial F_0(k_j)}{\partial \tilde{\Gamma}^*_{200}(k_m)}\right)_{\tilde{\Gamma}^0} \\
& \quad = \delta_{jm}\frac{\rho}{k_j}\tilde{C}^0_{200}(k_j) \\
& \qquad + \frac{\rho}{k_j}[2\tilde{C}^0_{000}(k_j) + \tilde{\Gamma}^0_{000}(k_j)]\left(\frac{\partial \tilde{C}_{000}(k_j)}{\partial \tilde{\Gamma}_{200}(k_m)}\right)_{\tilde{\Gamma}^{\mathrm{in}}} \\
& \qquad + \frac{\rho}{k_j}[2\tilde{C}^0_{200}(k_j) + \tilde{\Gamma}^0_{200}(k_j)]\left(\frac{\partial \tilde{C}_{200}(k_j)}{\partial \tilde{\Gamma}_{200}(k_m)}\right)_{\tilde{\Gamma}^{\mathrm{in}}}, \\
& \left(\frac{\partial F_1(k_j)}{\partial \tilde{\Gamma}^*_{200}(k_m)}\right)_{\tilde{\Gamma}^0} \\
& \quad = \delta_{jm}\left[-1 + \frac{\rho}{k_j}\tilde{C}^0_{220}(k_j)\right] \\
& \qquad + \frac{\rho}{k_j}[\tilde{C}^0_{000}(k_j) + \tilde{\Gamma}^0_{000}(k_j) + \tilde{C}^0_{220}]\left(\frac{\partial \tilde{C}_{200}(k_j)}{\partial \tilde{\Gamma}_{200}(k_m)}\right)_{\tilde{\Gamma}^{\mathrm{in}}} \\
& \qquad + \frac{\rho}{k_j}\tilde{C}^0_{200}(k_j)\left(\frac{\partial \tilde{C}_{000}(k_j)}{\partial \tilde{\Gamma}_{200}(k_m)}\right)_{\tilde{\Gamma}^{\mathrm{in}}},
\end{aligned} \tag{19}$$

$$\begin{aligned}\left(\frac{\partial F_1(k_j)}{\partial \tilde{\Gamma}^{*}_{000}(k_m)}\right)_{\tilde{\Gamma}^0} &= \delta_{jm}\frac{\rho}{k_j}\tilde{C}^{0}_{200}(k_j) \\ &\quad + \frac{\rho}{k_j}[\tilde{C}^{0}_{000}(k_j)+\tilde{C}^{0}_{220}(k_j)]\left(\frac{\partial \tilde{C}_{200}(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\tilde{\Gamma}^{in}} \\ &\quad + \frac{\rho}{k_j}\tilde{C}^{0}_{200}(k_j)\left(\frac{\partial \tilde{C}_{000}(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\tilde{\Gamma}^{in}},\end{aligned}$$

where δ_{jm} is the Kronecker delta. For the derivatives appearing on the right-hand side of (19), the superscript * has been dropped and the subscript $\tilde{\Gamma}^{in}$ in used rather than $\tilde{\Gamma}^0$. These result from linearization of the closure and the fact that all other harmonic coefficients are kept fixed.

Finally, the Hankel transforms for the first two harmonic coefficients needed in the evaluation of (18) and (19) are given by

$$\begin{aligned}\tilde{C}^{0}_{000}(k_j) &= \tilde{C}^{in}_{000}(k_j) + \sum_{m=1}^{J}\left(\frac{\partial \tilde{C}_{000}(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\tilde{\Gamma}^{in}} \\ &\quad \times [\tilde{\Gamma}^{0}_{000}(k_m)-\tilde{\Gamma}^{in}_{000}(k_m)] \\ &\quad + \sum_{m=1}^{J}\left(\frac{\partial \tilde{C}_{000}(k_j)}{\partial \tilde{\Gamma}_{200}(k_m)}\right)_{\tilde{\Gamma}^{in}}[\tilde{\Gamma}^{0}_{200}(k_m)-\tilde{\Gamma}^{in}_{200}(k_m)] \\ \tilde{C}^{0}_{200}(k_j) &= \tilde{C}^{in}_{200}(k_j) + \sum_{m=1}^{J}\left(\frac{\partial \tilde{C}_{200}(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\tilde{\Gamma}^{in}} \\ &\quad \times [\tilde{\Gamma}^{0}_{000}(k_m)-\tilde{\Gamma}^{in}_{000}(k_m)] \\ &\quad + \sum_{m=1}^{J}\left(\frac{\partial \tilde{C}_{200}(k_j)}{\partial \tilde{\Gamma}_{200}(k_m)}\right)_{\tilde{\Gamma}^{in}}[\tilde{\Gamma}^{0}_{200}(k_m)-\tilde{\Gamma}^{in}_{200}(k_m)].\end{aligned} \tag{20}$$

The formulae for the derivatives $\partial\tilde{C}_{p00}(k_j)/\partial\tilde{\Gamma}_{q00}(k_m)$, $p, q=0, 2$, appearing in (19) and (20) are given in Appendix A.

The overall GN method thus consists of two main iteration loops, and the details of the method are summarized as follows:

Construction of the New LC–OZ Equation (Outer Loop).

1. The initial approximation $\tilde{\Gamma}^{in}_{l_1l_2m}(k_j), j=1, 2, ..., N$, is chosen.
2. $\Gamma^{in}_{l_1l_2m}(r_i)$, $i=1, 2, ..., N$, are calculated from their Hankel transforms.
3. Given $u(12)$ and $B(12)$, $C^{in}_{l_1l_2m}(r_i)$ are calculated from (10).
4. The Hankel transforms $\tilde{C}^{in}_{l_1l_2m}(k_j)$ are calculated.
5. The right-hand side of Eqs. (9) are calculated as $\tilde{\Gamma}_{l_1l_2m}(k_j)$.
6. Test of convergence:

$$\frac{1}{N}\sum_{j=1}^{N}\sum_{l_1l_2m}[\tilde{\Gamma}_{l_1l_2m}(k_j)-\tilde{\Gamma}^{in}_{l_1l_2m}(k_j)]^2<\varepsilon.$$

If the inequality holds, convergence of the entire procedure has been achieved. If not, calculations are performed in the inner loop. In the latter case, set $\tilde{\Gamma}^{*}_{l_1l_2m}=\tilde{\Gamma}_{l_1l_2m}$, $j=1, 2, ..., N$.

Newton–Raphson iterations for primary solution components of the LC–OZ equation (first step of inner loop).

7. The harmonic coefficients $\phi^{in}_{l_1l_2m}(r_i)$ of $\phi^{in}(12)$ that appear in (14) are calculated by means of (13). The derivatives $(\partial\tilde{C}_{p00}(k_j)/\partial\tilde{\Gamma}_{q00}(k_m))_{\tilde{\Gamma}_{in}}$, $p, q=0, 2$, are calculated according to formulae (A7) in Appendix A.
8. Set $\tilde{\Gamma}^{0}_{l_1l_2m}(k_j)=\tilde{\Gamma}^{*}_{l_1l_2m}(k_j), j=1, 2, ..., N$.
9. The elements of the Jacobian matrix (19) are calculated, with $\tilde{C}^{0}_{000}(k_j)$ and $\tilde{C}^{0}_{200}(k_j)$ obtained by (20).
10. The set of $2J$ linear equations (18) is solved for $\tilde{\Gamma}^{*}_{000}(k_j)$, $\tilde{\Gamma}^{*}_{200}(k_j), j\leqslant J$.
11. Test of convergence:

$$\frac{1}{J}\sum_{j=1}^{J}[\tilde{\Gamma}^{*}_{000}(k_j)-\tilde{\Gamma}^{0}_{000}(k_j)]^2 + \frac{1}{J}\sum_{j=1}^{J}[\tilde{\Gamma}^{*}_{200}(k_j)-\tilde{\Gamma}^{0}_{200}(k_j)]^2<\varepsilon_{\mathrm{NR}}.$$

If the inequality is satisfied, convergence of the NR step has been achieved. In this case, the remaining $\tilde{\Gamma}^{*}_{l_1l_2m}(k_j)$ are calculated in the Picard step. If convergence has not been achieved the algorithm returns to step 8.

Picard iteration for secondary solution components of the LC–OZ equation (second step of inner loop).

12. New $\Gamma^{*}_{l_1l_2m}(r_i)$ are calculated as inverse Hankel transforms.
13. Corresponding $C^{*}_{l_1l_2m}(r_i)$ are calculated from (15) using $\Gamma^{*}_{l_1l_2m}(r_i)$ obtained in step 12.
14. The Hankel transforms $\tilde{C}^{*}_{l_1l_2m}(k_j)$ of $C^{*}_{l_1l_2m}(r_i)$ determined in the previous step are calculated.
15. The right-hand side of Eqs. (16) are calculated as $\tilde{\Gamma}^{*}_{l_1l_2m}(k_j)$.
16. Test of convergence:

$$\frac{1}{N}\sum_{j=1}^{N}\sum_{l_1l_2m}[\tilde{\Gamma}^{*}_{l_1l_2m}(k_j)-\tilde{\Gamma}^{0}_{l_1l_2m}(k_j)]^2<\varepsilon_{\mathrm{LC}},$$

where the inner summation is over all l_1, l_2, m. If the inequality is satisfied, convergence of the entire inner iteration loop has been achieved. The results are taken as the new initial estimates $\tilde{\Gamma}^{in}_{l_1l_2m}(k_j)$ and the algorithm returns to step 2 above. If convergence has not been achieved the algorithm returns to step 8.

5. RESULTS AND DISCUSSION

We compared the efficiency of our GN algorithm with the PF algorithm of Lado [11]. For illustration, the comparisons were made for a fluid of hard prolate ellipsoids of revolution having a length-to-breadth ratio of 3, and we considered the HNC closure, $B(12)=0$ in (3). The correlation functions were expanded in 28 spherical harmonics (000, 200, 220, 221, 222, ..., 664). The numerical calculations were carried out using $N=1024$ points with mesh-sizes $\Delta r=0.01$, $\Delta k=\pi/(N\Delta r)$. For the GN algorithm the number of values of the 000 and 200 harmonic coefficients obtained by the full NR method in the inner loop was $J=80$, and we used the convergence criteria $\varepsilon \sim 10^{-3}$, $\varepsilon_{\mathrm{NR}} \sim 10^{-2}$, and $\varepsilon_{\mathrm{LC}} \sim 5\cdot 10^{-3}$ in steps 6, 11, and 16, respectively. We used the same value of ε to indicate convergence of the PF algorithm. The integrals in Eq. (10) were calculated using the following product integration scheme: an adaptive extended Gaussian quadrature rule [30] with a maximum of 33 points was used for integration over $\cos\theta_1$ and $\cos\theta_2$; integration over ϕ_{12} was performed using an adaptive trapezoidal rule with a maximum of 64 points. (These integrals were evaluated only in the region of nonvanishing Boltzmann factor, $\exp[-\beta u(12)]$, determined according to the technique of [31]). The FORTRAN compiler on the HP-Apollo 9000/730 computer was used for all calculations.

Table I shows a comparison of the GN method with the PF method. We used the ideal gas initial estimate ($\tilde{\Gamma}^{in}_{l_1l_2m}(k_j)=0$) for the lowest density, and the results for the nearest lower density was taken as the initial estimate at higher densities. The times required for each method are compared in Table I, as are the number of iteration steps, N_{it}. For the GN method N_{it} is the number of times the LC–OZ equation is solved (at each of which the $C_{l_1l_2m}(r_i)$ harmonic coefficients must be calculated from Eq. (10)). Since most of the computation time for each method involves the evaluation of Eq. (10), the ratios of execution times to N_{it} are comparable for each method. At low densities our method is at least four times as fast as the PF method and at high densities it is approximately 10 times as fast.

TABLE I

Comparison of the Computer Time, t, and the Number of Iterations, N_{it}, of the GN and PF Methods for Numerically Solving the OZ Equation for the Hard Prolate Ellipsoid Fluid Using the HNC Approximation

	Present method		PF	
η	N_{it}	t/s	N_{it}	t/s
0.1	3	219	12	976
0.2	4	320	22	1958
0.3	5	431	39	2990
0.4	6	550	66	5250
0.45	5	492	69	5622

We remark that the system of hard prolate ellipsoids of revolution presents an especially difficult case for numerical algorithms. The fluid apparently undergoes an isotropic–nematic phase transition at a density slightly beyond the highest density in Table I (see [24] for further discussion of this point). We found both methods to be divergent beyond $\eta \sim 0.46$. For other systems we have studied [17–25], we have found both methods to converge slightly more rapidly. However, the relative convergence rates were observed to be similar to that in Table I. Also, similarly as noted elsewhere [15, 16], the PF method is sometimes divergent in cases for which the GN method converges. For example, for hard homonuclear diatomics, the GN method converges up to $\eta \sim 0.47$ [17, 18], whereas the PF method converges only up to $\eta \sim 0.42$ (depending on the closure used).

The GN method is much more efficient than the PF method, especially at high densities where the PF method may fail to converge. Although direct comparison of the GN method with other methods is difficult, we can make the following remarks. For simple fluids [6], the GN method has been found to be several times as fast as Gillan's method [5]. Since the method of Kinoshita and Harada [16] is the analogue of the latter method in the case of molecular fluids, we expect that the GN method is similarly better in this case.

Possible improvements to the GN method as presented here can be made by modifying the solution procedure used for the LC–OZ equation or by incorporating well-known numerical devices. One possibility with respect to the former is the use of more than two leading harmonic coefficients in the full NR step. However, the algebra involved becomes increasingly complex as this number increases. Another possibility is to vary the value of J in the NR step. Possibilities with respect to the latter include the use of relaxation parameters (e.g., [9, 15, 16]) in either the outer or inner iteration loops as well as the use of approximate Jacobian matrices in the NR step (e.g., [8, 9]). However, we expect that any of the above will lead to only relatively minor improvements in the basic GN method.

The GN method is potentially useful in the investigation of more complex theories of molecular fluids, such as the RHNC theory [32, 25] for soft-core linear molecules, the implementation of which requires the calculation of multiple numerical solutions of the OZ equation. Finally, we believe that the GN method can be successfully extended to the more difficult case of nonlinear molecular fluids. In addition, we believe that the general strategy of the method, as embodied in the sequential linearization of Eq. (11), can be successfully used in the numerical solution of other nonlinear integral equations.

APPENDIX A

Here we derive the expressions for the calculation of $\partial\tilde{C}_{p00}(k_j)/\partial\tilde{\Gamma}_{q00}(k_m)$, $p, q = 0, 2$ that appear in Eqs. (19) and (20). The derivatives of $\tilde{C}_{000}$ and $\tilde{C}_{200}$ with respect to $\tilde{\Gamma}_{000}$ and $\tilde{\Gamma}_{200}$ may be expressed as

$$\begin{aligned}
\frac{\partial\tilde{C}_{000}(k_j)}{\partial\tilde{\Gamma}_{000}(k_m)} &= \sum_{n=1}^{N} \frac{\partial\tilde{C}_{000}(k_j)}{\partial C_{000}(r_n)} \frac{\partial C_{000}(r_n)}{\partial\Gamma_{000}(r_n)} \frac{\partial\Gamma_{000}(r_n)}{\partial\tilde{\Gamma}_{000}(k_m)},\\
\frac{\partial\tilde{C}_{000}(k_j)}{\partial\tilde{\Gamma}_{200}(k_m)} &= \sum_{n=1}^{N} \frac{\partial\tilde{C}_{000}(k_j)}{\partial C_{000}(r_n)} \frac{\partial C_{000}(r_n)}{\partial\Gamma_{200}(r_n)} \frac{\partial\Gamma_{200}(r_n)}{\partial\tilde{\Gamma}_{200}(k_m)},\\
\frac{\partial\tilde{C}_{200}(k_j)}{\partial\tilde{\Gamma}_{000}(k_m)} &= \sum_{n=1}^{N} \frac{\partial\tilde{C}_{200}(k_j)}{\partial C_{200}(r_n)} \frac{\partial C_{200}(r_n)}{\partial\Gamma_{000}(r_n)} \frac{\partial\Gamma_{000}(r_n)}{\partial\tilde{\Gamma}_{000}(k_m)},\\
\frac{\partial\tilde{C}_{200}(k_j)}{\partial\tilde{\Gamma}_{200}(k_m)} &= \sum_{n=1}^{N} \frac{\partial\tilde{C}_{200}(k_j)}{\partial C_{200}(r_n)} \frac{\partial C_{200}(r_n)}{\partial\Gamma_{200}(r_n)} \frac{\partial\Gamma_{200}(r_n)}{\partial\tilde{\Gamma}_{200}(k_m)}.
\end{aligned} \tag{A1}$$

The derivatives $\partial\tilde{C}/\partial C$ on the right-hand sides may be calculated from the defining equations for the discrete Hankel transforms

$$\begin{aligned}
\tilde{C}_{000}(k_j) &= 4\pi\,\Delta r \sum_{i=1}^{N} C_{000}(r_i)\,k_j r_i j_0(k_j r_i),\\
\tilde{C}_{200}(k_j) &= 4\pi\,\Delta r \sum_{i=1}^{N} C_{200}(r_i)\,k_j r_i j_2(k_j r_i),
\end{aligned} \tag{A2}$$

where j_0 and j_2 are spherical Bessel functions,

$$\begin{aligned}
j_0(x) &= \sin(x)/x,\\
j_2(x) &= \frac{(3-x^2)\sin(x) - 3x\cos(x)}{x^3}.
\end{aligned} \tag{A3}$$

The derivatives $\partial C/\partial\Gamma$ may be obtained from the linearized closure equation (14), which becomes for the 000 and 200 harmonic coefficients

$$\begin{aligned}
C_{000}(r_i) &= C^{in}_{000}(r_i) + D_{00}(r_i)[\Gamma_{000}(r_i) - \Gamma^{in}_{000}(r_i)]\\
&\quad + D_{02}(r_i)[\Gamma_{200}(r_i) - \Gamma^{in}_{200}(r_i)],\\
C_{200}(r_i) &= C^{in}_{200}(r_i) + D_{20}(r_i)[\Gamma_{000}(r_i) - \Gamma^{in}_{000}(r_i)]\\
&\quad + D_{22}(r_i)[\Gamma_{200}(r_i) - \Gamma^{in}_{200}(r_i)],
\end{aligned} \tag{A4}$$

where

$$\begin{aligned}
D_{00}(r_i) &= \phi^{in}_{000}(r_i)\\
D_{02}(r_i) &= 2\phi^{in}_{200}(r_i)\\
D_{20}(r_i) &= \phi^{in}_{200}(r_i)\\
D_{22}(r_i) &= \phi^{in}_{000}(r_i) + \frac{\sqrt{20}}{7}\phi^{in}_{200}(r_i) + \frac{6}{7}\phi^{in}_{400}(r_i) + \phi^{in}_{220}(r_i).
\end{aligned} \tag{A5}$$

Similarly, the derivatives $\partial\Gamma/\partial\tilde{\Gamma}$ on the right-hand sides of (A1) are calculated from the defining equations for the discrete inverse Hankel transforms

$$\begin{aligned}
\Gamma_{000}(r_i) &= \frac{\Delta k}{2\pi^2} \sum_{j=1}^{N} \tilde{\Gamma}_{000}(k_j)\,k_j r_i j_0(k_j r_i),\\
\Gamma_{200}(r_i) &= \frac{\Delta k}{2\pi^2} \sum_{j=1}^{N} \tilde{\Gamma}_{200}(k_j)\,k_j r_i j_2(k_j r_i).
\end{aligned} \tag{A6}$$

Combining the above equations gives

$$\begin{aligned}
\frac{\partial\tilde{C}_{000}(k_j)}{\partial\tilde{\Gamma}_{000}(k_m)} &= \frac{2}{N}\sum_{n=1}^{N} D_{00}(r_n)\,k_j r_n j_0(k_j r_n)\,k_m r_n j_0(k_m r_n)\\
\frac{\partial\tilde{C}_{000}(k_j)}{\partial\tilde{\Gamma}_{200}(k_m)} &= \frac{2}{N}\sum_{n=1}^{N} D_{02}(r_n)\,k_j r_n j_0(k_j r_n)\,k_m r_n j_2(k_m r_n)\\
\frac{\partial\tilde{C}_{200}(k_j)}{\partial\tilde{\Gamma}_{000}(k_m)} &= \frac{2}{N}\sum_{n=1}^{N} D_{20}(r_n)\,k_j r_n j_2(k_j r_n)\,k_m r_n j_0(k_m r_n)\\
\frac{\partial\tilde{C}_{200}(k_j)}{\partial\tilde{\Gamma}_{200}(k_m)} &= \frac{2}{N}\sum_{n=1}^{N} D_{22}(r_n)\,k_j r_n j_2(k_j r_n)\,k_m r_n j_2(k_m r_n).
\end{aligned} \tag{A7}$$

APPENDIX B

In the text, the method of solution was described using spherical harmonics in the centre–centre molecular frame. In this frame only the harmonic coefficients $X_{l_1 l_2 m}$ with even l_1 and l_2 are nonvanishing. The modification of the GN algorithm for the site–site coordinate frame is straightforward. The leading harmonic coefficients in this frame are $\tilde{\Gamma}_{000}(k_j)$ and $\tilde{\Gamma}_{100}(k_j)$. For these the LC–OZ equation (17) in Fourier space becomes

$$\begin{aligned}
F_0(k_j) &= -\tilde{\Gamma}^*_{000}(k_j) + \frac{\rho}{k_j}\Big\{\tilde{C}^*_{000}(k_j)[\tilde{C}^*_{000}(k_j) + \tilde{\Gamma}^*_{000}(k_j)]\\
&\quad - \tilde{C}^*_{100}(k_j)[\tilde{C}^*_{100}(k_j) + \tilde{\Gamma}^*_{100}(k_j)]\\
&\quad + \sum_{l_3=2}^{\infty} (-1)^{l_3}\,\tilde{C}^*_{l_3 00}(k_j)[\tilde{C}^*_{l_3 00}(k_j) + \tilde{\Gamma}^*_{l_3 00}(k_j)]\Big\}\\
&= 0, \qquad j = 1, \ldots, J,\\
F_1(k_j) &= -\tilde{\Gamma}^*_{100}(k_j) + \frac{\rho}{k_j}\Big\{\tilde{C}^*_{100}(k_j)[\tilde{C}^*_{000}(k_j) + \tilde{\Gamma}^*_{000}(k_j)]\\
&\quad + \tilde{C}^*_{110}(k_j)[\tilde{C}^*_{100}(k_j) + \tilde{\Gamma}^*_{100}(k_j)]\\
&\quad - \sum_{l_3=2}^{\infty} (-1)^{l_3}\,\tilde{C}^*_{l_3 10}(k_j)[\tilde{C}^*_{l_3 00}(k_j) + \tilde{\Gamma}^*_{l_3 00}(k_j)]\Big\}\\
&= 0, \qquad j = 1, \ldots, J.
\end{aligned} \tag{B1}$$

The analogue of equation (18) is

$$
\begin{aligned}
&F_0^0(k_j) + \sum_{m=1}^{J} \left(\frac{\partial F_0(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\Gamma^0} [\tilde{\Gamma}_{000}(k_m) - \tilde{\Gamma}^0_{000}(k_m)] \\
&\quad + \sum_{m=1}^{J} \left(\frac{\partial F_0(k_j)}{\partial \tilde{\Gamma}_{100}(k_m)}\right)_{\Gamma^0} [\tilde{\Gamma}_{100}(k_m) - \tilde{\Gamma}^0_{100}(k_m)] \\
&= 0, \qquad j = 1, 2, \ldots, J, \\
&F_1^0(k_j) + \sum_{m=1}^{J} \left(\frac{\partial F_1(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\Gamma^0} [\tilde{\Gamma}_{000}(k_m) - \tilde{\Gamma}^0_{000}(k_m)] \\
&\quad + \sum_{m=1}^{J} \left(\frac{\partial F_1(k_j)}{\partial \tilde{\Gamma}_{100}(k_m)}\right)_{\Gamma^0} [\tilde{\Gamma}_{100}(k_m) - \tilde{\Gamma}^0_{100}(k_m)] \\
&= 0, \qquad j = 1, 2, \ldots, J,
\end{aligned}
\tag{B2}
$$

where the elements of the Jacobian matrix may be expressed from (B1) as

$$
\begin{aligned}
&\left(\frac{\partial F_0(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\Gamma^0} \\
&\quad = \delta_{jm}\left[-1 + \frac{\rho}{k_j}\tilde{C}^0_{000}(k_j)\right] \\
&\qquad + \frac{\rho}{k_j}[2\tilde{C}^0_{000}(k_j) + \tilde{\Gamma}^0_{000}(k_j)] \left(\frac{\partial \tilde{C}_{000}(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\Gamma^{in}} \\
&\qquad + \frac{\rho}{k_j}[2\tilde{C}^0_{100}(k_j) + \tilde{\Gamma}^0_{100}(k_j)] \left(\frac{\partial \tilde{C}_{100}(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\Gamma^{in}}, \\
&\left(\frac{\partial F_0(k_j)}{\partial \tilde{\Gamma}_{100}(k_m)}\right)_{\Gamma^0} \\
&\quad = \delta_{jm}\frac{\rho}{k_j}\tilde{C}^0_{100}(k_j) \\
&\qquad + \frac{\rho}{k_j}[2\tilde{C}^0_{000}(k_j) + \tilde{\Gamma}^0_{000}(k_j)] \left(\frac{\partial \tilde{C}_{000}(k_j)}{\partial \tilde{\Gamma}_{100}(k_m)}\right)_{\Gamma^{in}} \\
&\qquad + \frac{\rho}{k_j}[2\tilde{C}^0_{100}(k_j) + \tilde{\Gamma}^0_{100}(k_j)] \left(\frac{\partial \tilde{C}_{100}(k_j)}{\partial \tilde{\Gamma}_{100}(k_m)}\right)_{\Gamma^{in}},
\end{aligned}
\tag{B3}
$$

$$
\begin{aligned}
&\left(\frac{\partial F_0(k_j)}{\partial \tilde{\Gamma}_{100}(k_m)}\right)_{\Gamma^0} \\
&\quad = \delta_{jm}\left[-1 + \frac{\rho}{k_j}\tilde{C}^0_{110}(k_j)\right] \\
&\qquad + \frac{\rho}{k_j}[\tilde{C}^0_{000}(k_j) + \tilde{\Gamma}^0_{000}(k_j) + \tilde{C}^0_{110}(k_j)] \left(\frac{\partial \tilde{C}_{100}(k_j)}{\partial \tilde{\Gamma}_{100}(k_m)}\right)_{\Gamma^{in}} \\
&\qquad + \frac{\rho}{k_j}\tilde{C}^0_{100}(k_j) \left(\frac{\partial \tilde{C}_{000}(k_j)}{\partial \tilde{\Gamma}_{100}(k_m)}\right)_{\Gamma^{in}}, \\
&\left(\frac{\partial F_1(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\Gamma^0} \\
&\quad = \delta_{jm}\frac{\rho}{k_j}\tilde{C}^0_{100}(k_j) \\
&\qquad + \frac{\rho}{k_j}[\tilde{C}^0_{000}(k_j) + \tilde{C}^0_{110}(k_j)] \left(\frac{\partial \tilde{C}_{100}(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\Gamma^{in}} \\
&\qquad + \frac{\rho}{k_j}\tilde{C}^0_{100}(k_j) \left(\frac{\partial \tilde{C}_{000}(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\Gamma^{in}}.
\end{aligned}
$$

Finally, the analogue of Eqs. (20) is

$$
\begin{aligned}
\tilde{C}_{000}(k_j) &= \tilde{C}^{in}_{000}(k_j) + \sum_{m=1}^{J} \left(\frac{\partial \tilde{C}_{000}(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\Gamma^{in}} \\
&\quad \times [\tilde{\Gamma}_{000}(k_m) - \tilde{\Gamma}^{in}_{000}(k_m)] \\
&\quad + \sum_{m=1}^{J} \left(\frac{\partial \tilde{C}_{000}(k_j)}{\partial \tilde{\Gamma}_{100}(k_m)}\right)_{\Gamma^{in}} [\tilde{\Gamma}_{100}(k_m) - \tilde{\Gamma}^{in}_{100}(k_m)], \\
\tilde{C}_{100}(k_j) &= \tilde{C}^{in}_{100}(k_j) + \sum_{m=1}^{J} \left(\frac{\partial \tilde{C}_{100}(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)}\right)_{\Gamma^{in}} \\
&\quad \times [\tilde{\Gamma}_{000}(k_m) - \tilde{\Gamma}^{in}_{000}(k_m)] \\
&\quad + \sum_{m=1}^{J} \left(\frac{\partial \tilde{C}_{100}(k_j)}{\partial \tilde{\Gamma}_{100}(k_m)}\right)_{\Gamma^{in}} [\tilde{\Gamma}_{100}(k_m) - \tilde{\Gamma}^{in}_{100}(k_m)].
\end{aligned}
\tag{B4}
$$

The derivatives on the right-hand sides of Eqs. (B3) and (B4) are

$$
\begin{aligned}
\frac{\partial \tilde{C}_{000}(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)} &= \frac{2}{N}\sum_{n=1}^{N} D_{00}(r_n)\, k_j r_n j_0(k_j r_n)\, k_m r_n j_0(k_m r_n), \\
\frac{\partial \tilde{C}_{000}(k_j)}{\partial \tilde{\Gamma}_{100}(k_m)} &= \frac{2}{N}\sum_{n=1}^{N} D_{01}(r_n)\, k_j r_n j_0(k_j r_n)\, k_m r_n j_1(k_m r_n), \\
\frac{\partial \tilde{C}_{100}(k_j)}{\partial \tilde{\Gamma}_{000}(k_m)} &= \frac{2}{N}\sum_{n=1}^{N} D_{10}(r_n)\, k_j r_n j_1(k_j r_n)\, k_m r_n j_0(k_m r_n), \\
\frac{\partial \tilde{C}_{100}(k_j)}{\partial \tilde{\Gamma}_{100}(k_m)} &= \frac{2}{N}\sum_{n=1}^{N} D_{11}(r_n)\, k_j r_n j_1(k_j r_n)\, k_m r_n j_1(k_m r_n),
\end{aligned}
\tag{B5}
$$

where

$$
j_1(x) = \frac{\sin(x) - x\cos(x)}{x^2}
\tag{B6}
$$

and

$$
\begin{aligned}
D_{00}(r_i) &= \phi^{in}_{000}(r_i) \\
D_{01}(r_i) &= 2\phi^{in}_{100}(r_i) \\
D_{10}(r_i) &= \phi^{in}_{100}(r_i) \\
D_{11}(r_i) &= \phi^{in}_{000}(r_i) - \phi_{110}(r_i) + \frac{\sqrt{20}}{5}\phi^{in}_{200}(r_i).
\end{aligned}
\tag{B7}
$$

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