Numerical solution of structure integral equation theories for two-dimensional fluid mixtures

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A robust and efficient numerical method for solving the structure integral equation theories of two-dimensional (2D) fluid mixtures has been developed. It is a hybrid of the Newton–Raphson (NR) and Picard iterations. The Jacobian matrix is calculated analytically. With crude initial estimates, converged solutions are obtained in about 10–20 total NR iterations. The integral equations for 2D fluid mixtures with an arbitrary number of components can now be solved in practice. To illustrate the method, we have solved the Percus–Yevick equation for a binary hard-disc mixture which was previously treated with Monte Carlo simulation.

1. Introduction

Two-dimensional (2D) fluids have attracted attention as interesting model systems for various surface problems, such as monolayers of amphiphilic molecules on water [1], intercalation compounds [2] and monolayers of rare-gas mixtures adsorbed on a substrate [3]. For these studies, just as for those on three-dimensional (3D) fluids, the structure integral equation theories will offer a reliable approach. It may be noted, however, that while 2D systems are computationally less demanding then 3D ones in computer simulations, the opposite is true when the integral equation theories are used [4].

It has been shown that a 2D fluid is considerably more structured than its 3D counterpart [5]. This implies that numerical methods can be less stable. Further, the forward and back Hankel transforms needed in the solutions [4] are much more time-consuming than the fast Fourier transform. It is thus very desirable that the number of iterations in a numerical solution be kept as small as possible, making development of stable and efficient methods even more important for 2D fluids than for 3D ones.

Robust and very efficient methods [6–9] have been developed recently for solving numerically the nonlinear integral equation theories for 3D fluids, and they have been demonstrated for a wide range of problems. For 2D fluids, however, such numerical methods have not been investigated, although Pospisil and Malijevsky [10] have recently used an efficient algorithm for systems with circular symmetry in connection with their study of hard spheres near a hard cylinder of infinite length. No studies have been reported for 2D fluid mixtures.

The present article reports the development of a robust and efficient numerical

method for solving integral equation theories for 2D fluid mixtures. It is a hybrid of Newton–Raphson (NR) and Picard iterations which is obtained by extending to mixtures the procedure devised by Lado [4], and adapting to 2D fluids the algorithm developed by Labik *et al.* [8]. For the NR iteration, the Jacobian matrix is calculated analytically. As an application of the method, a solution is obtained for the Percus–Yevick (PY) equation for a binary hard-disc mixture which was previously treated with Monte Carlo (MC) simulation [3].

2. Numerical method

Experience with 3D fluids has shown that the hybrid algorithms [6–9] utilizing advantageous aspects of both the NR and Picard methods are the most efficient among reported methods. In particular, as long as bulk fluids are treated and the pair interactions are not angular dependent, the method developed by Labik *et al.* [8] (referred to here as the LMV method) appears to be the most attractive one. In this article, we adapt the LMV method to 2D fluid mixtures. The total number of components is arbitrary and denoted by NC.

The closure equation is given as

$$c_{n,i} = f(\gamma_{n,i}), \tag{1 a}$$

$$\gamma_{n,i} = h_{n.i} - c_{n,i}, \tag{1b}$$

where $c_n(r)$ and $h_n(r)$ are the direct and total correlation functions for pair n ($n = 1, \ldots, NP$; NP is the total number of distinct pairs and given by NP = (NC + 1)NC/2), and $c_{n,i}$ and $h_{n,i}$ denote values of the functions at point r_i ($i = 1, \ldots, N - 1$). Two popular approximations, the PY and the hypernetted chain (HNC), are expressed as

$$f(\gamma_{n,i}) = [\exp(-\beta u_{n,i}) - 1][\gamma_{n,i} + 1], \tag{2}$$

and

$$f(\gamma_{n,i}) = \exp(-\beta u_{n,i} + \gamma_{n,i}) - \gamma_{n,i} - 1, \tag{3}$$

respectively, where $u_n(r)$ is the pair potential and β has the usual meaning.

Linearizing the closure equation [8] yields

$$c_{n,i} = c_{n,i}^0 + \phi_{n,i}^0 (\gamma_{n,i} - \gamma_{n,i}^0), \tag{4}$$

$$\phi_{n.i}^0 = (df/d\gamma_{n,i})_{\gamma_{n,i} = \gamma_{n,i}^0}. \tag{5}$$

The forward Hankel transform [4] of equation (4) is

$$\tilde{c}_{n,i} = \tilde{c}_{n,j}^0 + (4\pi/K^2) \sum_{i=1}^{N-1} \phi_{n,i}^0 (\gamma_{n,i} - \gamma_{n,i}^0) J_0(\lambda_j \lambda_i / \lambda_N) / \{J_1(\lambda_i)\}^2, \tag{6 a}$$

$$\tilde{c}_{n,j} = (4\pi/K^2) \sum_{i=1}^{N-1} c_{n,i} J_0(\lambda_j \lambda_i / \lambda_N) / \{J_1(\lambda_i)\}^2, \tag{6 b}$$

where $J_m(x)$ is the Bessel function of the first kind of order m, $\lambda_1, \ldots, \lambda_N$ are the first

N positive roots of $J_0(x) = 0$, and $K = \lambda_{\mathrm{NS}}$ ($r_i = \lambda_i/\lambda_{\mathrm{NS}}$ and $r_{\mathrm{NS}} = 1$; NS is a sufficiently large integer). $\gamma_{n,i}$ is given as the back Hankel transform [4],

$$\gamma_{n,i} = \{1/(\pi R^2)\} \sum_{k=1}^{N-1} \tilde{\gamma}_{n,k} J_0(\lambda_k \lambda_i/\lambda_N)/\{J_1(\lambda_k)\}^2, \tag{7}$$

where $R = \lambda_N/\lambda_{\mathrm{NS}}$. Substituting equation (7) into equation (6 a) yields

$$\tilde{c}_{n,j} = \tilde{c}_{n,j}^0 + \sum_{k=1}^{N-1} \tilde{C}_{n,jk}(\tilde{\gamma}_{n,k} - \tilde{\gamma}_{n,k}^0), \tag{8}$$

$$\tilde{C}_{n,jk} = \{4/(KR)^2\} \sum_{i=1}^{N-1} \phi_{n,i}^0 J_0(\lambda_k \lambda_i/\lambda_N) J_0(\lambda_j \lambda_i/\lambda_N)/\{J_1(\lambda_k)J_1(\lambda_i)\}^2. \tag{9}$$

The Ornstein–Zernike (OZ) equation is expressed by

$$\tilde{\gamma}_{n,j} = F(\tilde{c}_{1,j}, \ldots, \tilde{c}_{\mathrm{NP},j}). \tag{10}$$

Here, the following functions are to be reduced to zero,

$$\tilde{\Psi}_{n,j} = \tilde{\gamma}_{n,j} - \tilde{\gamma}_{n,j}', \tag{11 a}$$

$$\tilde{\gamma}_{n,j}' = F(\tilde{c}_{1,j}, \ldots, \tilde{c}_{\mathrm{NP},j}), \tag{11 b}$$

where $\tilde{c}_{n,j}$ is given by equation (8). Then,

$$\begin{aligned} \partial\tilde{\Psi}_{n,j}/\partial\tilde{\gamma}_{m,l} &= \delta_{n,m}\delta_{j,l} - (\partial\tilde{\gamma}_{n,j}'/\partial\tilde{c}_{m,j})(\partial\tilde{c}_{m,j}/\partial\tilde{\gamma}_{m,l}) \\ &= \delta_{n,m}\delta_{j,l} - (\partial\tilde{\gamma}_{n,j}'/\partial\tilde{c}_{m,j})\tilde{C}_{m,jl}, \end{aligned} \tag{12}$$

where δ denotes Kronecker's delta, and we have used equation (8) for deriving $\partial\tilde{c}_{m,j}/\partial\tilde{\gamma}_{m,l}$.

The iteration proceeds as follows.

(1) Give the initial estimate $\gamma_{n,i}^0 (n = 1, \ldots, \mathrm{NP}; i = 1, \ldots, N - 1)$, and obtain $\tilde{\gamma}_{n,j}^0 (n = 1, \ldots, \mathrm{NP}; j = 1, \ldots, N - 1)$ by the forward Hankel transform.

(2) Calculate $c_{n,i}^0$ from the closure equation, and obtain $\tilde{c}_{n,j}^0$ by the forward Hankel transform. Also, calculate $\phi_{n,i}^0 (n = 1, \ldots, \mathrm{NP}; i = 1, \ldots, N - 1)$ from equation (5).

(3) Calculate $\tilde{C}_{n,jk}(n = 1, \ldots, \mathrm{NP}; j, k = 1, \ldots, M)$ from equation (9).

(4) Fixing $\tilde{\gamma}_{n,M+1}^0, \ldots, \tilde{\gamma}_{n,N-1}^0 (n = 1, \ldots, \mathrm{NP})$, obtain converged $\tilde{\gamma}_{n,1}, \ldots, \tilde{\gamma}_{n,M}$ by the NR method. More details are given below.

(5) Calculate $\tilde{\gamma}_{n,M+1}, \ldots, \tilde{\gamma}_{n,N-1}$ from equation (10) where $\tilde{c}_{n,j}$ are replaced by $\tilde{c}_{n,j}^0 (n = 1, \ldots, \mathrm{NP}; j = M + 1, \ldots, N - 1)$.

(6) Set $\tilde{\gamma}_{n,j}^0 := \tilde{\gamma}_{n,j}(n = 1, \ldots, \mathrm{NP}; j = 1, \ldots, N - 1)$. Obtain $\gamma_{n,i}^0$ by the back Hankel transform and return to step (2).

The NR iteration in step (4) is performed to find the $M \times \mathrm{NP}$ variables, $\tilde{\gamma}_{n,1}, \ldots, \tilde{\gamma}_{n,M}$, which make $M \times \mathrm{NP}$ functions, $\tilde{\Psi}_{n,j}$, almost exactly zero. The elements of the Jacobian matrix are given by equation (12). The partial derivatives $\partial\tilde{\gamma}_{n,j}'/\partial\tilde{c}_{m,j}$ can be obtained as explained in the appendix. We note that the calculation of $\tilde{C}_{n,jk}$ is needed only for $j, k = 1, \ldots, M$. The starting guesses are $\tilde{\gamma}_{n,j} = \tilde{\gamma}_{n,j}^0$.

Thus, the iterative loop comprises two subloops: the inner loop of the NR iteration and the outer loop of the Picard iteration. The two subloops are considered converged once

$$E_{IN} = \sum_{n=1}^{NP} \sum_{j=1}^{M} |\tilde{\Psi}_{n,j}|/(M \times NP) < \varepsilon_{IN} \tag{13}$$

and

$$E_{OUT} = \sum_{n=1}^{NP} \sum_{j+M+1}^{N-1} |(\tilde{\gamma}_{n,j} - \tilde{\gamma}_{n,j}^0)/\tilde{\gamma}_{n,j}|/\{(N - M - 1) \times NP\} < \varepsilon_{OUT} \tag{14}$$

are satisfied, respectively.

N and NS must be sufficiently large (e.g. $N = 500$ and NS $= 50$). The set of values, $\lambda_i (i = 1, \ldots, N - 1)$, $J_0(\lambda_k \lambda_i/\lambda_N)$ $(k,i = 1, \ldots, N - 1)$ and $J_1(\lambda_i)$ $(i = 1, \ldots, N - 1)$, can be calculated readily [11] and is used as part of the input data. For mixtures of hard-disc potential systems, care must be taken because the points r_i are not equally spaced [4]. We note, however, that the points are 'almost' equally spaced and the following treatment is sufficient. The diameter for each component is specified by giving an even integer $NI(I = 1, \ldots, NC)$. One of the components, component 1, is chosen as the reference and $N1$ is set to NS. Then, the diameter of component I, σ_I/σ_1, is equal to λ_I/λ_1. The diameter of a distinct pair $\sigma_{IJ}/\sigma_1(\sigma_{IJ} = (\sigma_I + \sigma_J)/2)$ is set to λ_{NIJ}/λ_1 where NIJ $= (NI + NJ)/2$. Here, as an example is a set of values for binary mixtures: $N = 500$, $N1 = $ NS $= 50$, $N2 = 40$, $\sigma_2/\sigma_1 = 0.7990$ and $\sigma_{12}/\sigma_1 = 0.8995$. The relation, $\sigma_{12} = (\sigma_1 + \sigma_2)/2$, is satisfied. On the other hand, σ_2/σ_1 is not exactly equal to $N2/N1$, but this causes no serious problem because these two parameters are 'almost' exactly equal (the discrepancy in the above example is only $\sim -0.13\%$ and this is comparable with the error of the numerical treatment).

3. Numerical examples

The efficiency of the proposed numerical method will now be demonstrated. The tolerances ε_{IN} and ε_{OUT} are set at 10^{-3} and 10^{-5}, respectively. At least one iteration is performed in the inner loop regardless of the value of ε_{IN}. When the outer loop is converged, ε_{IN} is also smaller than 10^{-5}. There is no need to calculate the Jacobian matrix at every step [7, 9]. In the present study, the calculation of the matrix is skipped when ε_{IN} is smaller than 10^{-2}. N, NS and M were set at 500, 50 and 30, respectively.

Table 1.   Convergence properties of the proposed numerical method (NC $= 1$). ρ is the number density. σ is the hard-disc diameter in cases 1 and 2. In cases 3–5, the pair potential is given by $u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$.

Case	$\rho\sigma^2$	$1/(\beta\varepsilon)$	PY L_{OUT}	PY L_{IN}	HNC L_{OUT}	HNC L_{IN}
1	0·5		4	8	5	11
2	0·7		6	11	11	18
3	0·7	1·2	7	13	8	16
4	0·7	0·9	10	16	8	14
5	0·7	0·7	17	24	10	17

Table 2. Convergence properties of the proposed numerical method for ternary hard disc mixtures (NC = 3) combined with the PY theory. ρ_I and σ_I denote the number density and the hard disc diameter of component I, respectively. The diameter ratios are $\sigma_2/\sigma_1 = 0.7990$ and $\sigma_3/\sigma_1 = 1.2010$.

Case	$\rho_1\sigma_1^2$	$\rho_2\sigma_1^2$	$\rho_3\sigma_1^2$	L_{OUT}	L_{IN}
6	0.25	0.15	0.10	6	10
7	0.25	0.25	0.25	10	16
8	0.50	0.30	0.10	15	21

Numerical calculations were first performed for five cases as summarized in table 1. Hard discs are treated in cases 1 and 2, and Lennard-Jones potential systems are tested in cases 3–5. The ideal gas was taken as the initial estimate in cases 1–3. The initial estimate in the other cases was the converged result obtained at the nearest higher value of $1/(\beta\varepsilon)$. L_{IN} and L_{OUT} denote the number of total iterations needed in the inner and outer loops, respectively. It is worthwhile to note that the converged result was obtained readily for hard discs combined with HNC theory even at $\rho\sigma^2 = 0.9$. At this density the fluid is highly structured, and the first, second and third peak values of $g(r)$ (the pair correlation function) are 11·6, 2·86 and 1·76, respectively. The converged result was never obtained by the conventional numerical method [4]. We also note that as many as 1200 iterations were needed in another study [2]. Our conclusion is that the proposed numerical method is much more robust and efficient than the conventional Picard method.

In table 2, three cases of ternary hard-disc mixtures (NC = 3) are treated with PY theory. $N1$, $N2$ and $N3$ were set at 50, 40 and 60, respectively. Then, $\sigma_2/\sigma_1 = 0.7990$, $\sigma_3/\sigma_1 = 1.2010$, $\sigma_{12} = 0.8995$, $\sigma_{13} = 1.1005$ and $\sigma_{23} = 1.0000$. The initial estimate was the ideal gas. It should be noted that the total packing fraction is considerably elevated in case 8. Nevertheless, it was easy to achieve convergence. The convergence properties are thus very good even for multicomponent systems.

4. PY result for binary hard disc mixtures

Barrat *et al.* [3] reported MC simulation data for binary hard-disc mixtures. We solve the PY equation for these systems and compare the result with their MC data. To our knowledge, this is the first time that an integral equation theory is solved for 2D fluid mixtures. The thermodynamic condition chosen was the following: $\alpha = \sigma_1/\sigma_2 = 0.7$, $x = 0.546$ and $\eta = 0.55$, where σ_I, x and η are the hard-disc diameter of component I, mole fraction of component 2 and the total packing fraction, respectively. $N1$ and $N2$ were set at 42 and 60, respectively. Then, $\alpha = 0.6988$ (the discrepancy is only $\sim -0.17\%$) and $\sigma_{12} = 0.8494$. With $M = 30$ and the initial estimate of the ideal gas, L_{OUT} and L_{IN} were only 9 and 14, respectively.

The direct correlation and partial pair correlation functions calculated from PY theory are shown in figures 1 and 2, respectively. It is interesting that the qualitative aspects of $c_{IJ}(r)$ observed in figure 1 are the same as those in the first figure of [3] that were obtained from the scaling theory. Each $g_{IJ}(r)$ in figure 2 has a shoulder on the small-r side of the second peak. Since the numerical data for $g_{IJ}(r)$ from the MC simulation are not available, we cannot plot the data in figure 2. Comparing $g_{IJ}(r)$ in figure 2 with the plot given in the fourth figure of [3], however, we may conclude
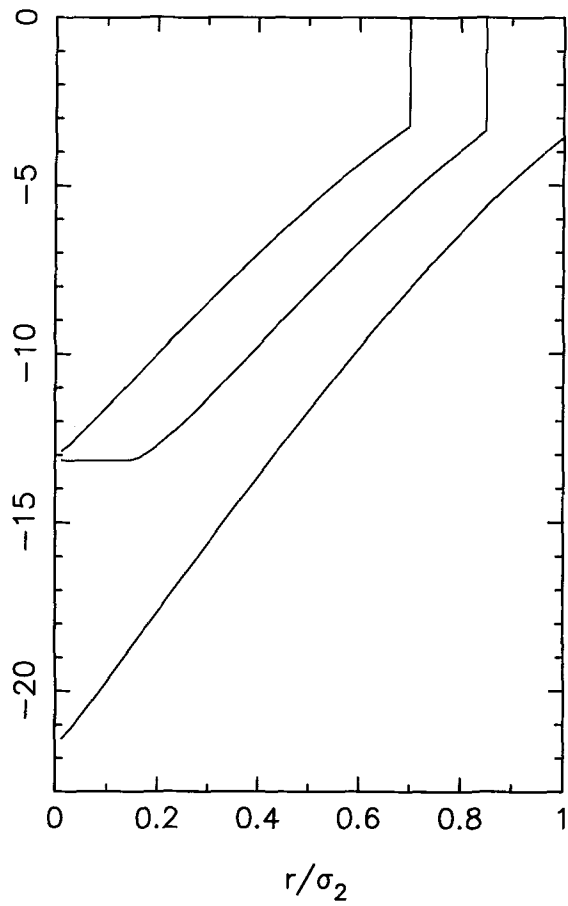
M. Kinoshita and F. Lado

Figure 1. Direct correlation functions $c_{IJ}(r)$ calculated from the PY theory for a binary hard-disc mixture.
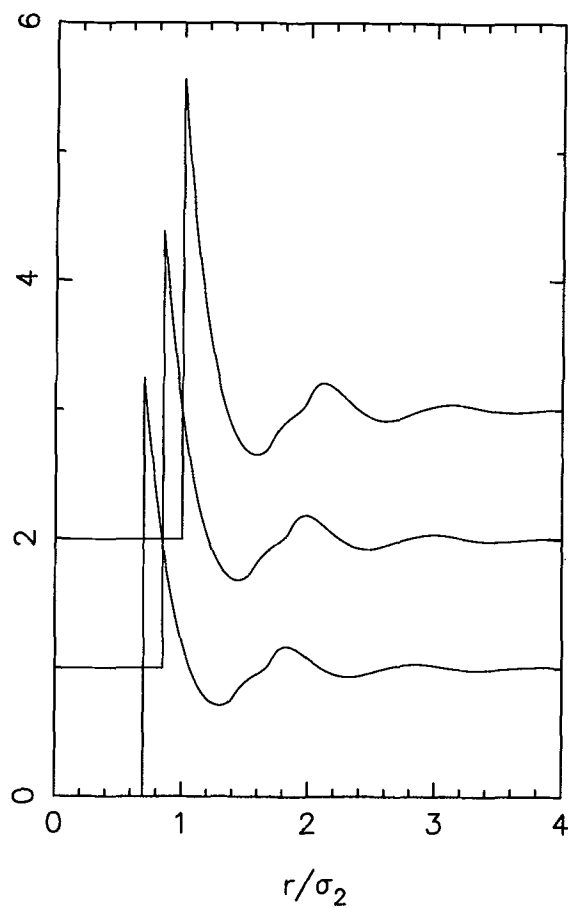
Figure 2.   Partial pair correlation functions $g_{ij}(r)$, plotted as $g_{11}(r)$, $1 + g_{12}(r)$ and $2 + g_{22}(r)$, calculated from PY theory for a binary hard-disc mixture.

that the PY result agrees well with the MC result. The reduced pressure calculated from PY theory coupled with the virial equation is 4·31 which is in close agreement with the MC value 4·55.

5. Conclusion

An efficient method has been developed for numerical solution of structure integral equation theories for 2D fluid mixtures. It is a hybrid of the NR and Picard iterations. The elements of the Jacobian matrix are calculated analytically. Its robustness and high efficiency has been demonstrated by numerical experiments. The integral equations for 2D fluid mixtures with an arbitrary number of components can now be solved in practice.

We have solved the PY equation for a binary hard-disc mixture which was previously treated by MC simulation [3]. It appears that the PY result is in close agreement with the MC data.

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Appendix

Calculation of partial derivatives, $\partial \tilde{\gamma}'_{n,j}/\partial \tilde{c}_{m,j}$

It is convenient to express the OZ equation in the following matrix form,

$$\gamma'_j = (\gamma'_j + c_j)\rho c_j, \tag{A 1}$$

where γ'_j is a symmetrical matrix whose (I, J) element is $\tilde{\gamma}'_{IJ,j}$ $(I,J = 1,\ldots,\text{NC};$ $\text{NP} = (\text{NC} + 1)\text{NC}/2)$, c_j is also a symmetrical matrix whose (I, J) element is $\tilde{c}_{IJ,j}$, and ρ is a diagonal matrix whose diagonal elements are number densities of components ρ_I. The relations among $\tilde{\gamma}'_{n,j}(n = 1,\ldots,\text{NP})$ and $\tilde{\gamma}'_{IJ,j}$ or those among $\tilde{c}'_{n,j}$ and $\tilde{c}'_{IJ,j}$ are straightforward. For NC = 2, for example, NP = 3 and $\tilde{\gamma}'_{1,j} = \tilde{\gamma}'_{11,j}$, $\tilde{\gamma}'_{2,j} = \tilde{\gamma}'_{12,j} = \tilde{\gamma}'_{21,j}$ and $\tilde{\gamma}'_{3,j} = \tilde{\gamma}'_{22,j}$. It follows that

$$\gamma'_j = c_j \rho c_j Q_j^{-1}, \tag{A 2a}$$

$$Q_j = I - \rho c_j, \tag{A 2b}$$

where I is the identity matrix and Q_j^{-1} is the inverse matrix of Q_j. It can be shown that

$$\mathrm{d}\gamma'_j = (\mathrm{d}c_j)\rho c_j Q_j^{-1} + (c_j + \gamma'_j)\rho(\mathrm{d}c_j)Q_j^{-1}. \tag{A 3}$$

Then, analytical expressions for the partial derivatives are obtained as follows:

$$\partial \tilde{\gamma}'_{IJ,j}/\partial \tilde{c}_{KK,j} = \delta_{I,K}\rho_K \sum_L (c_j)_{KL}(Q_j^{-1})_{LJ}$$

$$+ (c_j + \gamma'_j)_{IK}\rho_K(Q_j^{-1})_{KJ}, \tag{A 4}$$

$$\partial \tilde{\gamma}'_{IJ,j} / \partial \tilde{c}_{KL,j} = \delta_{I,K} \rho_L \sum_M (c_j)_{LM} (Q_j^{-1})_{MJ}$$

$$+ \delta_{I,L} \rho_K \sum_M (c_j)_{KM} (Q_j^{-1})_{MJ}$$

$$+ (c_j + \gamma'_j)_{IK} \rho_K (Q_j^{-1})_{LJ}$$

$$+ (c_j + \gamma'_j)_{IL} \rho_L (Q_j^{-1})_{KJ}, \text{ for } K \neq L, \tag{A 5}$$

where $(c_j)_{KL}$, for example, denotes the (K, L) element of the matrix c_j. Equations (A 2), (A 4) and (A 5) allow us to calculate analytically the partial derivatives, $\partial \tilde{\eta}'_{n,j} / \partial \tilde{c}_{m,j}$.

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