Analytical solution of the multidensity OZ equation for polymerizing fluid

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An analytical solution of the multidensity Ornstein-Zernike equation together with the Percus-Yevick-like approximation for the model of polymerizing fluid is obtained in closed form. The solution is illustrated by its application to the sticky shielded shell model of Stell; it can be also easily utilized for a number of other simple models of polymerizing fluids.

I. INTRODUCTION

Recently much effort has been focused on the development of integral-equation theories for the description of equilibrium properties of polymer fluids [1–5]. Perhaps the most promising among them are those which are based on the extension of the Wertheim's theory for associating fluids [1,4–6]. However most of the applications of these theories are restricted to the case in which particles are associating on the dimer level only [7–12].

In the present study we obtain an analytical solution of the multidensity Ornstein-Zernike (OZ) equation closed be Percus-Yevick-like (PY) closure conditions [4] for the shielded sticky shell (SSS) model for polymerization [13]. The solution carried out for this model is also applicable to a number of other models of polymerizing fluids proposed recently [1,5,15] and their extensions, especially a two-species version of the totally flexible two-site model of Wertheim [15] in the case in which each site is a sticky point randomly positioned on the surface of an interaction shell of radius L. In this sticky two-point (S2P) model [15] the shell coincides with the surface of the interaction shell defined by the repulsive core of the monomers, but if instead it is shielded by a repulsive core of unit radius, with $\frac{1}{2} \leq L \leq 1$, our treatment of a two-species version of the resulting model, which we shall call a shielded sticky two-point (SS2P) model, is virtually identical to our SSS development applied to the range $\frac{1}{2} \leq L \leq \frac{1}{\sqrt{3}}$, except for some minor changes. In this range, each monomer in the SSS model can be associated with at most two neighboring monomers, which is also the case in the SS2P model for all L such that $\frac{1}{2} \leq L \leq 1$. In fact, for $\frac{1}{2} \leq L \leq \frac{1}{\sqrt{3}}$, a two-species version of the SS2P model and SSS model are thermodynamically identical (for $L = 1$ the SS2P models reduce to the S2P models). We expect, on the basis of previous studies [12,14], that the PY-type closure used below will be especially accurate for the SS2P model with L near or at 1; for the SSS model its expected accuracy is harder for us to judge.

II. THE MODEL

The SSS model consists of a two-component mixture of species a and b of the same size and densities $\rho^a = \rho^b = \rho$ with a hard-sphere interaction between particles of the same species and both hard-sphere and sticky interaction between particles of different species. In this model the sticky interaction is presented by the sticky shell placed inside the hard-core region at a distance $\frac{1}{2}L$ from the center of the hard sphere, which we take to be of unit diameter [13,14]. The stickiness is introduced as a limiting case of the finite attraction under the constraint that the second virial coefficient for the total potential is kept constant. In this limit the Mayer function $f_{ij}(r)$ is given by

$$f_{ij}(r) = f_{ij}^{(hs)}(r) + \frac{K_0}{4\pi L^2}(1-\delta_{ij})\delta(r-L) \tag{1}$$

where i and j stand for the species of the particles and take the values a and b, $f_{ij}^{(hs)}(r)$ is the hard-sphere Mayer function, K_0 is the parameter of stickiness, and we assume $\frac{1}{2} \leq L \leq 1$. One can easily see that the structure of clusters formed by this type of the model depends on the specific choice of the value of L [4,14].

III. INTEGRAL EQUATION AND CLOSURE CONDITIONS

The multidensity integral equation formalism for the model in question has been developed in [4]. Therefore we shall omit any details of the diagrammatical analysis and derivation of the OZ equation and its closure and present here only the final result for the particular case of the three-density version of the theory. This particular three-density case is very similar to that proposed recently in [5].

The three-density OZ for the present model can be written in the matrix form as follows

$$\hat{\mathbf{H}}(k) = \hat{\mathbf{C}}(k) + \hat{\mathbf{C}}(k)\boldsymbol{\sigma}\hat{\mathbf{H}}(k) \tag{2}$$

where $[\boldsymbol{\sigma}]_{ij} = \delta_{ij}\boldsymbol{\sigma}_i$ and the matrices $\hat{\mathbf{H}}(k)$ and $\hat{\mathbf{C}}(k)$ contain the elements which are the Fourier transform of the elements of the matrices $\mathbf{H}(r)$ and $\mathbf{C}(r)$, respectivly. Here $[\mathbf{H}(r)]_{ij} =$

$\mathbf{h}_{ij}(r)$ and $[\mathbf{C}(r)]_{ij} = \mathbf{c}_{ij}(r)$. In turn $\mathbf{h}_{ij}(r)$, $\mathbf{c}_{ij}(r)$, and $\boldsymbol{\sigma}_i$ are the matrices which take the form

$$\mathbf{h}_{ij}(r) = \begin{pmatrix} h^{ij}_{00}(r) & h^{ij}_{01}(r) & h^{ij}_{02}(r) \\ h^{ij}_{10}(r) & h^{ij}_{11}(r) & h^{ij}_{12}(r) \\ h^{ij}_{20}(r) & h^{ij}_{21}(r) & h^{ij}_{22}(r) \end{pmatrix}, \qquad \boldsymbol{\sigma}_i = \begin{pmatrix} \sigma^i_2 & \sigma^i_1 & \sigma^i_0 \\ \sigma^i_1 & \sigma^i_0 & 0 \\ \sigma^i_0 & 0 & 0 \end{pmatrix}$$

where the lower indices α and β in σ^i_α and in partial correlation functions $h^{ij}_{\alpha\beta}(r)$ and $h^{ij}_{\alpha\beta}(r)$ denote the bonded states of the correspondent particle. The case of $\alpha = 0$ corresponds to unbonded particle, $\alpha = 1$ to a singly bonded particle and $\alpha = 2$ to a doubly bonded particle. The density parameters σ^i_α is related to the densities ρ_α of α-times bonded particles by

$$\sigma^i_0 = \sigma_0 = \rho_0, \qquad \sigma^i_1 = \sigma_1 = \rho_0 + \rho_1, \qquad \sigma^i_2 = \sigma_2 = \rho_0 + \rho_1 + \rho_2 \tag{3}$$

where the total density $\rho^i = \rho$ of the particles of species i is $\rho = \sigma^i_2 = \rho_0 + \rho_1 + \rho_2$. Here, since a and b species are indistinguishable, $\rho^a_\alpha = \rho^b_\alpha = \rho_\alpha$ and $\sigma^a_\alpha = \sigma^b_\alpha = \sigma_\alpha$

In this study we are using the PY-like closure conditions [4,6], which for the present model reads

$$y^{ij}_{\alpha\beta}(r) = g^{ij}_{\alpha\beta}(r) - c^{ij}_{\alpha\beta}(r) \tag{4}$$

where $g^{ij}_{\alpha\beta}(r) = h^{ij}_{\alpha\beta}(r) + \delta_{i0}\delta_{j0}$ and the functions $y^{ij}_{\alpha\beta}(r)$ are the analogues of the regular cavity correlation functions and are related to the partial pair correlation functions $g^{ij}_{\alpha\beta}(r)$ by

$$g^{ij}_{\alpha\beta}(r) = e^{ij}_{hs}(r)[y^{ij}_{\alpha\beta}(r) + (1-\delta_{0\alpha})(1-\delta_{0\beta})(1-\delta_{ij})B_{\alpha-1\beta-1}\delta(r-L)] \tag{5}$$

Here $e^{ij}_{hs}(r)$ is the Boltzmann factor for the hard-sphere interaction and $B_{\alpha\beta} = \frac{K_0}{4\pi L^2} y^{ij}_{\alpha\beta}(L)$.

Combining (4) and (5) and using the properties of the hard-sphere potential we have

$$h^{ij}_{\alpha\beta}(r) = -\delta_{0\alpha}\delta_{0\beta} + (1-\delta_{0\alpha})(1-\delta_{0\beta})(1-\delta_{ij})B_{\alpha-1\beta-1}\delta(r-L), \qquad for \quad r < 1 \tag{6}$$

$$c^{ij}_{\alpha\beta}(r) = 0, \qquad for \quad r > 1 \tag{7}$$

Finally the relation between the densities ρ_α, ρ and K_0 is defined by [4]

$$\rho_0^2(I_{00}+I_{01})+\rho_0\rho_1 I_{00}-\rho_1=0 \tag{8}$$

$$\rho_0^3(I_{11}+I_{10})+\rho_0^2\rho_1 I_{10}+\frac{1}{2}\rho_1^2+\rho_1\rho_0+\rho_0^2-\rho\rho_0=0 \tag{9}$$

where $I_{\alpha\beta}=K_0 y^{ab}_{\alpha\beta}(L)$.

IV. ANALYTICAL SOLUTION OF THE THREE-DENSITY OZ EQUATION

The OZ equation (2) together with the PY-like closure conditions (6), (7) and relation between the densities (8) and (9) form a closed set of equations to be solved. Our solution of this set of equations is based upon Baxter factorization technique [16]. The general scheme of the analytical solution is similar to that presented in [17] and [12]. Since all the direct correlation functions are finite ranged the factorization version of the OZ equation (2) can be used

$$-rh^{ij}_{\alpha\beta}(r)=[q^{ij}_{\alpha\beta}(r)]'-2\pi\sum_k\sum_{\gamma\delta}\sigma_{\gamma\delta}\int_0^1 q^{ik}_{\alpha\gamma}(t)(r-t)h^{kj}_{\delta\beta}(|r-t|)dt \tag{10}$$

$$-rc^{ij}_{\alpha\beta}(r)=[q^{ij}_{\alpha\beta}(r)]'-2\pi\sum_k\sum_{\gamma\delta}\sigma_{\gamma\delta}\partial/\partial r\int_0^{1-r} q^{ik}_{\gamma\alpha}(t)q^{kj}_{\delta\beta}(r+t)dt \tag{11}$$

where $\sigma_{\gamma\delta}$ is the correspondent element of the matrix $\boldsymbol{\sigma}=\boldsymbol{\sigma}_a=\boldsymbol{\sigma}_b$ and the Baxter functions $q^{ij}_{\alpha\beta}(r)$ is equal zero for $r>1$.

An analytical expression for $q^{ij}_{\alpha\beta}(r)$ at $0<r<1$ can be obtained now by analyzing equation (10) in this range and utilizing the closure relations (6) and (7) together with the boundary conditions

$$q^{ij}_{\alpha\beta}(1^{+1})=0 \tag{12}$$

This analysis can be simplified by using the properties of the symmetry of the model. Since both species a and b are indistinguishable, any of the two-particle function which involves the particles of species a is equal to that which involves the particles of species b. Therefore for simplicity we introduce the following notation

$$\phi^{(l)}_{\alpha\beta}(r) = \begin{cases} \phi^{aa}_{\alpha\beta}(r) = \phi^{bb}_{\alpha\beta}(r), & l = 0; \\ \phi^{ab}_{\alpha\beta}(r) = \phi^{ba}_{\alpha\beta}(r), & l = 1; \end{cases}$$

where ϕ denotes any of the two-particle function.

Due to specific properties of the density matrix $\boldsymbol{\sigma}$ the solution of equation (10) for the q-function can be obtained in three steps. First, equation (10) can be solved for the function $q^{(l)}_{\alpha 0}(r)$

$$q^{(l)}_{\alpha 0}(r) = \frac{1}{2}a_\alpha r^2 + b_\alpha r + c_\alpha, \qquad for \quad 0 < r < 1 \tag{13}$$

where

$$a_\alpha = \delta_{\alpha 0} - 2\pi \sum_\beta \sigma_\beta \sum_{l=0}^{1} \int_0^1 q^{(l)}_{\alpha\, 2-\beta}(t)\, dt, \quad b_\alpha = 2\pi \sum_\beta \sigma_\beta \sum_{l=0}^{1} \int_0^1 t q^{(l)}_{\alpha\, 2-\beta}(t)\, dt \tag{14}$$

and c_α is the constant of integration.

Since the coefficients a_α and b_α are independent of l and due to the boundary conditions (12) we have $q^{(0)}_{\alpha 0}(r) = q^{(1)}_{\alpha 0}(r)$.

Next, considering (10) for $\beta = 1$, we arrive at a set of differential-difference equations for the function $q^{(l)}_{\alpha 1}(r)$

$$-[q^{(l)}_{\alpha 1}(r)]' = 2\pi L(\sigma_1 B_{00} + \sigma_0 B_{10})[q^{(l)}_{\alpha 0}(r+L) - q^{(l)}_{\alpha 0}(r-L)] +$$

$$+2\pi L\sigma_0 B_{00}[q^{(1-l)}_{\alpha 1}(r+L) - q^{(1-l)}_{\alpha 1}(r-L)] + LB_{00}\delta_{l1}\delta(r-L) \tag{15}$$

Here the functions $q^{(l)}_{\alpha 0}(r)$ are known from the previous step. Solution of this set of equations can be obtained in a similar way as that used in [12]. We separate the total interval [0,1] into three subintervals $I_1 = [0, 1-L]$, $I_2 = [1-L, L]$, $I_3 = [L, 1]$. In each of these subintervals we get

$$q^{(l)}_{\alpha 1}(r) = A_{\alpha 1,n}r^2 + B_{\alpha 1,n}r + C_{\alpha 1,n} + u^{(l)}_{\alpha 1,n}\cos\omega r + v^{(l)}_{\alpha 1,n}\sin\omega r, \quad r \in I_n, \quad n = 1,3, \tag{16}$$

$$q_{\alpha 1}^{(l)}(r) = C_{\alpha 1,2}^{(l)} \qquad r \in I_2. \qquad (17)$$

Here $\omega = 2\pi\sigma_0 B_{00} L$, $C_{\alpha 1,2}^{(l)}$ is the constant of integration and $u_{\alpha 1,n}^{(l)}$ and $v_{\alpha 1,n}^{(l)}$ are related to the constants of integration $u_\alpha^{(l)}$ and $v_\alpha^{(l)}$ by

$$u_{\alpha 1,1}^{(l)} = u_\alpha^{(l)}, \qquad v_{\alpha 1,1}^{(l)} = v_\alpha^{(l)},$$

$$u_{\alpha 1,3}^{(l)} = -u_\alpha^{(1-l)} \sin\omega L - v_\alpha^{(1-l)} \cos\omega L, \qquad v_{\alpha 1,3}^{(l)} = u_\alpha^{(1-l)} \cos\omega L - v_\alpha^{(1-l)} \sin\omega L \qquad (18)$$

All the rest of the coefficients in (16) and (17) can be presented in terms of the parameters which appeares in the expression (13) for the function $q_{\alpha 0}^{(l)}(r)$

$$A_{\alpha 1,1} = -\frac{1}{2}\lambda a_\alpha, \qquad A_{\alpha 1,3} = A_{\alpha 1,1},$$

$$B_{\alpha 1,1} = -\frac{\lambda}{\omega}(a_\alpha + \omega b_\alpha), \qquad B_{\alpha 1,3} = \frac{\lambda}{\omega}(a_\alpha - \omega b_\alpha),$$

$$C_{\alpha 1,1} = \frac{\lambda}{\omega^2}[a_\alpha - (a_\alpha L + b_\alpha)\omega - c_\alpha \omega^2], \quad C_{\alpha 1,3} = \frac{\lambda}{\omega^2}[a_\alpha - (a_\alpha L - b_\alpha)\omega - c_\alpha \omega^2]$$

where $\lambda = (\sigma_1 B_{00} + \sigma_0 B_{10})/(\sigma_0 B_{00})$.

Finally, for $\beta = 2$ we have

$$-[q_{\alpha 2}^{(l)}(r)]' = 2\pi L(\sigma_1 B_{01} + \sigma_0 B_{11})[q_{\alpha 0}^{(l)}(r+L) - q_{\alpha 0}^{(l)}(r-L)] +$$

$$+ 2\pi L\sigma_0 B_{01}[q_{\alpha 1}^{(1-l)}(r+L) - q_{\alpha 1}^{(1-l)}(r-L)] + LB_{01}\delta_{1l}\delta(r-L) \qquad (19)$$

where the functions $q_{\alpha 0}^{(l)}(r)$ and $q_{\alpha 1}^{(l)}(r)$ are defined by (13), (16) and (17).

Solution of this set of equation follows immediately after the integration in (19) is performed in each of the subintervals I_n

$$q_{\alpha 2}^{(l)}(r) = D_{\alpha 2,n} r^3 + A_{\alpha 2,n} r^2 + B_{\alpha 2,n} r + C_{\alpha 2,n}^{(l)} +$$

$$+ u_{\alpha 1,n}^{(l)} \cos\omega r + v_{\alpha 1,n}^{(l)} \sin\omega r, \qquad r \in I_n, \; n = 1, 3, \qquad (20)$$

$$q^{(l)}_{\alpha 2}(r) = C^{(l)}_{\alpha 2,2}, \qquad r \in I_2. \tag{21}$$

Here $C^{(l)}_{\alpha 2,2}$ are the constants of integration and the expressions for all the rest of the coefficients are

$$D_{\alpha 2,1} = -\frac{1}{3}\pi L\sigma_0 P a_\alpha, \qquad D_{\alpha 2,3} = -D_{\alpha 2,1},$$

$$A_{\alpha 2,1} = -\pi L\sigma_0[P(b_\alpha + a_\alpha L) + \frac{\lambda}{\omega}B_{01}a_\alpha], \quad A_{\alpha 2,3} = \pi L\sigma_0[P(b_\alpha - a_\alpha L) - \frac{\lambda}{\omega}B_{01}a_\alpha],$$

$$B_{\alpha 2,1} = -2\pi L\sigma_0[P(\frac{1}{2}a_\alpha L^2 + b_\alpha L + c_\alpha) + \frac{\lambda}{\omega}B_{01}(\frac{a_\alpha}{\omega} + b_\alpha)],$$

$$B_{\alpha 2,3} = 2\pi L\sigma_0[P(\frac{1}{2}a_\alpha L^2 - b_\alpha L + c_\alpha) + \frac{\lambda}{\omega}B_{01}(\frac{a_\alpha}{\omega} + b_\alpha)],$$

$$u^{(l)}_{\alpha 2,1} = \frac{B_{01}}{B_{00}}u^{(l)}_\alpha, \qquad v^{(l)}_{\alpha 2,1} = \frac{B_{01}}{B_{00}}v^{(l)}_\alpha,$$

$$u^{(l)}_{\alpha 2,3} = -\frac{B_{01}}{B_{00}}(u^{(1-l)}_\alpha \sin\omega L + v^{(1-l)}_\alpha \cos\omega L), \qquad v^{(l)}_{\alpha 2,3} = \frac{B_{01}}{B_{00}}(u^{(1-l)}_\alpha \cos\omega L - v^{(1-l)}_\alpha \sin\omega L),$$

where $P = (B_{00}B_{11} - B_{01}B_{10})/B_{00}$.

The expressions (13), (16), (17), (20) and (21) for the Baxter function $q^{(l)}_{ij}(r)$ involves, via $B_{\alpha\beta}$, the values of the cavity correlation functions $y^{(1)}_{ij}(L)$ for i and $j < 2$, the densities ρ_0 and ρ_1, and the set of the constants a_α, b_α, c_α, $C^{(l)}_{\alpha 1,2}$, $C^{(l)}_{\alpha 2,n}$, $u^{(l)}_\alpha$, $v^{(l)}_\alpha$. Expression for $y^{(1)}_{ij}(L)$ follows from the closure conditions (4) in which (10) and (11) have been used

$$Ly^{(1)}_{00}(L) = a_0 L + b_0 - 2\pi\xi_{00}(L), \qquad Ly^{(1)}_{10}(L) = a_1 L + b_1 - 2\pi\xi_{10}(L)$$

$$Ly^{(1)}_{11}(L) = 2\pi L\sigma_0 B_{00}[q^{(0)}_{10}(0)\lambda + q^{(0)}_{11}(0)] - 2\pi\xi_{11}(L) \tag{22}$$

where the functions $\xi_{00}(L)$, $\xi_{10}(L)$ and $\xi_{11}(L)$ are presented in the Appendix. The densities ρ_0 and ρ_1 can be obtained from the set of equations (8) and (9). Expressions for a_α and b_α (14) together with the boundary conditions imposed on the function $q^{(l)}_{\alpha\beta}(r)$

$$q^{(l)}_{\alpha\beta}(1) = 0 \tag{23}$$

$$q^{(l)}_{\alpha\beta}(1 - L^+) = q^{(l)}_{\alpha\beta}(1 - L^-), \qquad \beta = 1, 2 \tag{24}$$

$$q^{(l)}_{\alpha\beta}(L^-) = q^{(l)}_{\alpha\beta}(L^+) - (1-\delta_{\alpha 0})(1-\delta_{\beta 0})\delta_{l1}B_{\alpha-1\,\beta-1}L \tag{25}$$

form a set of forty five linear equations for the unknown constants a_α, b_α, c_α, $C^{(l)}_{\alpha 1,2}$, $C^{(l)}_{\alpha 2,n}$, $u^{(l)}_\alpha$, $v^{(l)}_\alpha$. After some algebra this set of equations can be presented as three sets of linear equations coupled by the relation between the densities (8) and (9) and by the expressions (22) for the cavity correlation functions $y^{(1)}_{\alpha\beta}(L)$

$$\mathbf{z}_\alpha \mathbf{M}_\alpha = \mathbf{R}_\alpha \tag{26}$$

where

$$\mathbf{z}_\alpha = (a_\alpha,\, b_\alpha,\, c_\alpha,\, C^{(0)}_{\alpha 1,2},\, C^{(1)}_{\alpha 1,2},\, C^{(0)}_{\alpha 2,1},\, C^{(1)}_{\alpha 2,1},\, C^{(0)}_{\alpha 2,2},$$
$$C^{(1)}_{\alpha 2,2},\, C^{(0)}_{\alpha 2,3},\, C^{(1)}_{\alpha 2,3},\, u^{(0)}_\alpha,\, u^{(1)}_\alpha,\, v^{(0)}_\alpha,\, v^{(1)}_\alpha)$$

and the elements of the matrices $\mathbf{M}_\alpha$ and $\mathbf{R}_\alpha$ are given in the Appendix.

Thus the problem of solving the OZ equation (2) has been reduced to the solution of the set of algebraic equations (8), (9), (22) and (26). With this aim an iterative method similar to that used in [12] can be utilized. The set is first turned into a set of linear equations using as an input estimates for the values of the densities and of the cavity correlation functions. We start from the high-temperature limit, which give $\rho_0 = \rho$, $\rho_1 = 0$, $y^{(l)}_{00}(L) = y_{PY}(L)$, $y^{(l)}_{01}(L) = y^{(l)}_{11}(L) = 0$. Here $y_{PY}(L)$ is the cavity correlation function obtained from the regular PY approximation. Solution of the sets of linear equations (26) for $\alpha = 1, 2$ *and* 3 is used then to get a new estimates of $y^{(l)}_{\alpha\beta}(L)$ from (22) and ρ_0, ρ_1 from the solution of the set of nonlinear equations (8) and (9).

Finally, the partial pair correlation functions $g^{ab}_{\alpha\beta}(r)$ can be calculated by utilizing the iterative method of Perram [18]. With this aim equation (10) is to be used. For the sake of numerical convenience we present equation (10) in the following form

$$rg^{ij}_{\alpha\beta}(r) = \delta_{\beta 0}(a_\alpha + b_\alpha) + 2\pi(1-\delta_{\beta 0})\sum_k \sum_{\gamma\delta}(1-\delta_{kj})(1-\delta_{\delta 0})\sigma_{\gamma\delta}B_{\delta-1\,\beta-1}q^{ik}_{\alpha\gamma}(r-L)+$$

$$+2\pi \sum_k \sum_{\gamma\delta} \sigma_{\gamma\delta} \int_0^{r-1} q^{ik}_{\alpha\gamma}(t)(r-t) g^{kj}_{\delta\beta}(r-t)\, dt, \quad for \;\; r > 1 \tag{27}$$

Application of the Perram scheme requires the knowledge of the contact values of $g^{ij}_{\alpha\beta}(r)$. The latter follow from equation (27) at $r = 1^+$

$$g^{ij}_{\alpha\beta}(1^+) = (a_\alpha + b_\beta)\delta_{\beta 0} + 2\pi(1-\delta_{\beta 0}) \sum_k \sum_{\gamma\delta} (1-\delta_{kj})(1-\delta_{\delta 0})\sigma_{\gamma\delta} B_{\delta-1\, \beta-1} q^{ik}_{\alpha\gamma}(1-L) \tag{28}$$

The total pair distribution function $g_{ij}(r)$ is related to the partial correlation functions $g^{ij}_{\alpha\beta}(r)$ by

$$g_{ij}(r) = \sum_{\gamma\delta} \sigma_{0\gamma} g^{ij}_{\gamma\delta}(r) \sigma_{\delta 0} \tag{29}$$

V. APPENDIX

$$\xi_{00}(L) = 2\sum_{\alpha\beta} \sigma_{\alpha\beta} \Big\{ \frac{1}{8} a_\alpha a_\beta (1-L)^4 + \frac{1}{3}[\frac{1}{2} a_\alpha (a_\beta L + b_\beta) + b_\alpha a_\beta](1-L)^3 +$$
$$+ \frac{1}{2}[b_\alpha(a_\beta L + b_\beta) + c_\alpha a_\beta](1-L)^2 + c_\alpha(a_\beta L + b_\beta)(1-L) \Big\},$$

$$\xi_{10}(L) = 2\sum_{\alpha\beta} \sigma_{\alpha\beta} \Big\{ \frac{1}{4} A_{\alpha 1,1} a_\beta (1-L)^4 + \frac{1}{3}[A_{\alpha 1,1}(a_\beta L + b_\beta) + B_{\alpha 1,1} a_\beta](1-L)^3 +$$
$$+ \frac{1}{2}[B_{\alpha 1,1}(a_\beta L + b_\beta) + C_{\alpha 1,1} a_\beta](1-L)^2 + C_{\alpha 1,1}(a_\beta L + b_\beta)(1-L) \Big\} +$$
$$+ \sum_{l=0}^{1} \sum_{\alpha\beta} \sigma_{\alpha\beta} \Big\{ \frac{u^{(l)}_\alpha a_\beta}{\omega}[\frac{t^{(1)}_c}{\omega} + (1-L)t^{(1)}_s - \frac{1}{\omega}] + \frac{v^{(l)}_\alpha a_\beta}{\omega}[\frac{t^{(1)}_s}{\omega} - (1-L)t^{(1)}_c] +$$
$$+ \frac{(a_\beta L + b_\beta)}{\omega}[u^{(l)}_\alpha t^{(1)}_s - v^{(l)}_\alpha (t^{(1)}_c - 1)] \Big\},$$

$$\xi_{11}(L) = 2\sum_{\alpha\beta} \sigma_{\alpha\beta} \Big\{ \frac{1}{2} A_{\alpha 1,1} A_{\beta 1,3} (1-L)^4 + \frac{1}{3}[A_{\alpha 1,1}(2A_{\beta 1,3} L + B_{\beta 1,3}) + 2B_{\alpha 1,1} A_{\beta 1,3}](1-L)^3 +$$
$$+ \frac{1}{2}[B_{\alpha 1,1}(2A_{\beta 1,3} L + B_{\beta 1,3}) + 2C_{\alpha 1,1} A_{\beta 1,3}](1-L)^2 + C_{\alpha 1,1}(2A_{\beta 1,3} L + B_{\beta 1,3})(1-L) \Big\} +$$

$$+\sum_{l=0}^{1}\sum_{\alpha\beta}\sigma_{\alpha\beta}\Big\{A_{\alpha 1,1}u_\beta^{(l)}[((1-L)^2-\frac{2}{\omega^2})t_s^{(1)}+\frac{2(1-L)}{\omega}t_c^{(1)}]+A_{\alpha 1,1}v_\beta^{(l)}[(\frac{2}{\omega^2}-(1-L)^2)t_c^{(1)}+\frac{2(1-L)}{\omega}t_s^{(1)}-\frac{2}{\omega^2}]+$$

$$+B_{\alpha 1,1}\{u_\beta^{(l)}[\frac{t_c^{(1)}}{\omega}+(1-L)t_s^{(1)}-\frac{1}{\omega}]+v_\beta^{(l)}[\frac{t_s^{(1)}}{\omega}-(1-L)t_c^{(1)}]\}+C_{\alpha 1,1}[u_\beta^{(l)}t_s^{(1)}-v_\beta^{(l)}(t_c^{(1)}-1)]+$$

$$+\frac{2A_{\beta 1,3}}{\omega}\{u_\alpha^{(l)}[\frac{t_c^{(1)}}{\omega}+(1-L)t_s^{(1)}-\frac{1}{\omega^2}]+v_\alpha^{(l)}[\frac{t_s^{(1)}}{\omega}-(1-L)t_c^{(1)}]\}+$$

$$+\frac{2A_{\beta 1,3}L+B_{\beta 1,3}}{\omega}[u_\alpha^{(l)}t_s^{(1)}-v_\alpha^{(l)}(t_c^{(1)}-1)]+$$

$$+\frac{1}{4}u_\alpha^{(l)}\{u_\beta^{(l)}[t_s^{(2)}+2\omega(1-L)]+v_\beta^{(l)}(1-t_c^{(2)})\}+\frac{1}{4}v_\alpha^{(l)}\{u_\beta^{(l)}(1-t_c^{(2)})+v_\beta^{(l)}[2\omega(1-L)-t_s^{(2)}]\}\Big\}.$$

Here

$$t_s^{(1)}=\sin\omega(1-L),\qquad t_s^{(2)}=\sin 2\omega(1-L),$$

$$t_c^{(1)}=\cos\omega(1-L),\qquad t_c^{(2)}=\cos 2\omega(1-L).$$

The nonzero elements of the matrices $\mathbf{M}_\alpha$ and $\mathbf{R}_\alpha$ are

$$M_\alpha(1,1)=1+\frac{2}{3}\pi\sigma_2+4\pi\lambda\sigma_1(1-L)[\frac{1}{6}(L-2L^2-2)+\frac{1}{\omega}(\frac{2}{\omega}-L)]+$$

$$+2\pi\sigma_0(1-L)[\frac{1}{6}\kappa L(L^2-L+2)+\frac{1}{3}(\kappa L+\frac{\eta}{\omega})(L-2L^2-2)+L(L^2\kappa+\frac{2\eta}{\omega^2}],$$

$$M_\alpha(1,2)=2\pi\sigma_2-4\pi\sigma_1\lambda(1-L)-4\pi\sigma_0(1-L)(\kappa L+\frac{2\eta}{\omega}),\quad M_\alpha(1,3)=4\pi\sigma_2+8\pi(1-L)(\kappa\sigma_0L-\lambda\sigma_1),$$

$$M_\alpha(1,4)=2\pi\sigma_1(2L-1),\ \ M_\alpha(1,5)=2\pi\sigma_1(2L-1),\ \ M_\alpha(1,6)=2\pi\sigma_0(1-L),\ \ M_\alpha(1,7)=2\pi\sigma_0(1-L),$$

$$M_\alpha(1,8)=2\pi\sigma_0(2L-1),\ \ M_\alpha(1,9)=2\pi\sigma_0(2L-1),\ \ M_\alpha(1,10)=M_\alpha(1,6),\ \ M_\alpha(1,11)=M_\alpha(1,7),$$

$$M_\alpha(1,12)=\frac{2\pi}{\omega}(t_s^{(1)}-t_c^{(1)}+1)(\sigma_1+\frac{B_{01}}{B_{00}}\sigma_0),\qquad M_\alpha(1,13)=\frac{2\pi}{\omega}(t_s^{(1)}-t_c^{(1)}+1)(\sigma_1+\frac{B_{01}}{B_{00}}\sigma_0),$$

$$M_\alpha(1,14)=\frac{2\pi}{\omega}(1-t_s^{(1)}-t_c^{(1)})(\sigma_1+\frac{B_{01}}{B_{00}}\sigma_0),\qquad M_\alpha(1,15)=\frac{2\pi}{\omega}(1-t_s^{(1)}-t_c^{(1)})(\sigma_1+\frac{B_{01}}{B_{00}}\sigma_0),$$

$$M_\alpha(2,1)=\frac{1}{2}\pi\sigma_2+4\pi\sigma_1\lambda(1-L)[\frac{1}{\omega^2}-\frac{1}{4}(1-L+2L^2)]+$$

$$+4\pi\sigma_0(1-L)[L(L^2\kappa+\frac{2\eta}{\omega^2})-\frac{1}{2}(\kappa L+\frac{\eta}{\omega})(1-L+2L^2)+\frac{1}{3}\kappa L(L^2-L+1)],$$

$$M_\alpha(2,2)=-1+\frac{4}{3}\pi\sigma_2-4\pi\sigma_1\lambda(1-L)[\frac{1}{3}(2L^2-L+2)-\frac{L}{\omega}]+$$

$$4\pi\sigma_0(1-L)[\frac{1}{2}\kappa L(2-L+L^2)-\frac{2}{3}(L\kappa+\frac{\eta}{\omega})(2-L+2L^2)],$$

$$M_\alpha(2,3) = 2\pi\sigma_2 - 4\pi\sigma_1\lambda(1-L) + 8\pi\sigma_0\kappa L(1-L),$$

$$M_\alpha(2,4) = \pi\sigma_1(2L-1),\quad M_\alpha(2,5) = \pi\sigma_1(2L-1),\quad M_\alpha(2,6) = \pi\sigma_0(1-L)^2,\quad M_\alpha(2,7) = \pi\sigma_0(1-L)^2,$$

$$M_\alpha(2,8) = \pi\sigma_0(2L-1),\quad M_\alpha(2,9) = \pi\sigma_0(2L-1),\quad M_\alpha(2,10) = \pi\sigma_0(1-L^2),\quad M_\alpha(2,11) = \pi\sigma_0(1-L^2),$$

$$M_\alpha(2,12) = \frac{2\pi}{\omega^2}(\sigma_1 + \frac{B_{01}}{B_{00}}\sigma_0)[t_c^{(1)}(1-\omega) + t_s^{(1)}(\omega - \omega L + 1) - 1 + \omega L],\quad M_\alpha(2,13) = M_\alpha(2,12),$$

$$M_\alpha(2,14) = \frac{2\pi}{\omega^2}(\sigma_1 + \frac{B_{01}}{B_{00}}\sigma_0)[t_s^{(1)}(1+\omega) + t_c^{(1)}(-\omega + \omega L - 1) + 1],\quad M_\alpha(2,15) = M_\alpha(2,14),$$

$$M_\alpha(3,1) = \frac{1}{2},\quad M_\alpha(3,2) = 1,\quad M_\alpha(3,3) = 1,$$

$$M_\alpha(4,1) = \lambda[\frac{1}{\omega}(1 - L + \frac{1}{\omega}) - \frac{1}{2}],\quad M_\alpha(4,2) = \lambda(\frac{1}{\omega} - 1),\quad M_\alpha(4,3) = -\lambda,$$

$$M_\alpha(4,13) = t_s^{(1)},\quad M_\alpha(4,15) = -t_c^{(1)},$$

$$M_\alpha(5,1) = \lambda[\frac{1}{\omega}(1 - L + \frac{1}{\omega}) - \frac{1}{2}],\quad M_\alpha(5,2) = \lambda(\frac{1}{\omega} - 1),\quad M_\alpha(5,3) = -\lambda,$$

$$M_\alpha(5,12) = t_s^{(1)},\quad M_\alpha(5,14) = -t_c^{(1)},$$

$$M_\alpha(6,1) = \lambda(\frac{1}{\omega^2} - \frac{1}{2}L^2),\quad M_\alpha(6,2) = \lambda(\frac{1}{\omega} - L),\quad M_\alpha(6,3) = -\lambda,\quad M_\alpha(6,4) = -1,\quad M_\alpha(6,15) = -1,$$

$$M_\alpha(7,1) = \lambda(\frac{1}{\omega^2} - \frac{1}{2}L^2),\quad M_\alpha(7,2) = \lambda(\frac{1}{\omega} - L),\quad M_\alpha(7,3) = -\lambda,\quad M_\alpha(7,5) = -1,\quad M_\alpha(7,14) = -1,$$

$$M_\alpha(8,1) = \lambda[\frac{1}{\omega}(\frac{1}{\omega} - 1) - \frac{1}{2}(1-L)^2],\quad M_\alpha(8,2) = -\lambda(1 - L + \frac{1}{\omega}),\quad M_\alpha(8,3) = -\lambda,$$

$$M_\alpha(8,4) = -1,\quad M_\alpha(8,12) = t_c^{(1)},\quad M_\alpha(8,14) = t_s^{(1)},$$

$$M_\alpha(9,1) = \lambda[\frac{1}{\omega}(\frac{1}{\omega} - 1) - \frac{1}{2}(1-L)^2],\quad M_\alpha(9,2) = -\lambda(1 - L + \frac{1}{\omega}),\quad M_\alpha(9,3) = -\lambda,$$

$$M_\alpha(9,5) = -1,\quad M_\alpha(9,13) = t_c^{(1)},\quad M_\alpha(9,15) = t_s^{(1)},$$

$$M_\alpha(10,1) = \kappa(\frac{1}{3} - L + L^2) + \frac{\eta}{\omega}(\frac{2}{\omega} - 1),\quad M_\alpha(10,2) = \kappa(1-2L) - \frac{2\eta}{\omega},\quad M_\alpha(10,3) = 2\kappa,$$

$$M_\alpha(10,10) = 1,\quad M_\alpha(10,13) = \frac{B_{01}}{B_{00}}t_s^{(1)},\quad M_\alpha(10,15) = -\frac{B_{01}}{B_{00}}t_c^{(1)}$$

$$M_\alpha(11,1) = \kappa(\frac{1}{3} - L + L^2) + \frac{\eta}{\omega}(\frac{2}{\omega} - 1),\quad M_\alpha(11,2) = \kappa(1-2L) - \frac{2\eta}{\omega},\quad M_\alpha(11,3) = 2\kappa,$$

$$M_\alpha(11,11) = 1,\quad M_\alpha(11,12) = \frac{B_{01}}{B_{00}}t_s^{(1)},\quad M_\alpha(11,14) = -\frac{B_{01}}{B_{00}}t_c^{(1)}$$

$$M_\alpha(12,1) = \frac{1}{3}\kappa L^3 + \frac{\eta L}{\omega}(\frac{2}{\omega} - L),\quad M_\alpha(12,2) = -L[\kappa L(L+2) + \frac{2\eta}{\omega}],\quad M_\alpha(12,3) = 2\kappa L,$$

$$M_\alpha(12,8)=-1,\quad M_\alpha(12,10)=1,\quad M_\alpha(12,15)=-\frac{B_{01}}{B_{00}}$$

$$M_\alpha(13,1)=\frac{1}{3}\kappa L^3+\frac{\eta L}{\omega}(\frac{2}{\omega}-L),\quad M_\alpha(13,2)=-L[\kappa L(L+2)+\frac{2\eta}{\omega}],\quad M_\alpha(13,3)=2\kappa L,$$

$$M_\alpha(13,9)=-1,\quad M_\alpha(13,11)=1,\quad M_\alpha(13,14)=-\frac{B_{01}}{B_{00}}$$

$$M_\alpha(14,1)=(1-L)[\frac{1}{3}\kappa(1+L+L^2)+\frac{\eta}{\omega}(1-L+\frac{2}{\omega})],\quad M_\alpha(14,2)=(1-L)[\kappa(1+L)+\frac{2\eta}{\omega}],$$

$$M_\alpha(14,3)=2\kappa(1-L),\quad M_\alpha(14,6)=-1,\quad M_\alpha(14,8)=1,\quad M_\alpha(14,12)=-\frac{B_{01}}{B_{00}}t_c^{(1)},$$

$$M_\alpha(14,14)=-\frac{B_{01}}{B_{00}}t_s^{(1)},$$

$$M_\alpha(15,1)=(1-L)[\frac{1}{3}\kappa(1+L+L^2)+\frac{\eta}{\omega}(1-L+\frac{2}{\omega})],\quad M_\alpha(15,2)=(1-L)[\kappa(1+L)+\frac{2\eta}{\omega}],$$

$$M_\alpha(15,3)=2\kappa(1-L),\quad M_\alpha(15,7)=-1,\quad M_\alpha(15,9)=1,\quad M_\alpha(15,13)=-\frac{B_{01}}{B_{00}}t_c^{(1)},$$

$$M_\alpha(15,15)=-\frac{B_{01}}{B_{00}}t_s^{(1)},$$

$$R_\alpha(1)=\delta_{0\alpha},\quad R_\alpha(7)=-(1-\delta_{\alpha 0})B_{\alpha-1\,0}L,\quad R_\alpha(13)=-(1-\delta_{\alpha 0})B_{\alpha-1\,1}L$$

Here

$$\kappa=\pi LP\sigma_0,\quad \eta=\pi L\lambda\sigma_0$$

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