

# Solution of the polymer Percus–Yevick approximation for the multicomponent totally flexible sticky two-point model of polymerizing fluid

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The analytic solution of the polymer Percus–Yevick approximation for the multicomponent version of the totally flexible sticky two-point model of Wertheim is obtained in closed form. The model consists of an  $n$ -component mixture of hard spheres with two sticky points of the type A and B randomly placed on the surface of each hard sphere. The solution of the problem has been reduced to solving a set of  $5n$  algebraic equations. An iterative scheme of the solution of this set of equations is proposed. © 1995 American Institute of Physics.

## I. THE MODEL AND CLOSURE CONDITIONS

In recent years several off-lattice theories for the polymer fluids, based on the integral-equation techniques developed for the fluids of small molecules, have been proposed. These include the polymer reference interaction site model (PRISM) theory<sup>1</sup> and its extensions,<sup>2,3</sup> Percus–Yevick (PY) theory extended to the polymer fluids in,<sup>4</sup> multidensity integral equation theory<sup>5</sup> and its extension<sup>6</sup> and theory based on the polymer Born–Green–Yvon (PBGY) equation.<sup>7,8</sup> The application of the PRISM theory is focused mainly on the description of the long-chain polymer molecules, while the rest of the theories mentioned above appear to be reasonably successful in the description of the relatively short chains.

In two recent studies,<sup>9,10</sup> Wertheim's multidensity integral-equation theory<sup>5</sup> and its extension<sup>6</sup> have been applied to study two closely related models for polymerizing fluids. In Ref. 9 the totally flexible sticky two-point (S2P) model of Wertheim<sup>11</sup> was studied using the polymer PY (PPY) approximation,<sup>5</sup> while in Ref. 10 an analytical solution of a quite similar PY-like approximation<sup>6</sup> for the shielded sticky shell model<sup>12</sup> was presented. It was found that the predictions of the PPY approximation for the structural properties of the totally flexible S2P model were in good agreement with the corresponding computer simulation results.

In this study we present the analytical solution of the PPY approximation for the multicomponent version of the totally flexible S2P model. The model consists of the  $n$ -component mixture of hard spheres of species  $a=1,\dots,n$  with diameters  $R_a$  and densities  $\rho_a$ . Each of the hard sphere has two sticky points, A and B, randomly placed on the surface. The pair potential for this model consists of the hard-sphere term  $U_{ab}^{\text{HS}}(r)$  and a term describing sticky interaction

$$U_{ab}(r) = U_{ab}^{\text{HS}}(r) + \sum_{KL} U_{KL}^{ab}(12), \quad (1)$$

where 1 and 2 denote the positions and orientations of the two particles,

$$U_{ab}^{\text{HS}}(r) = \infty, \quad r < R_{ab} \\ = 0, \quad r > R_{ab},$$

$R_{ab} = \frac{1}{2}(R_a + R_b)$ ,  $U_{KL}^{ab}(12)$  is the site–site potential of sticky interaction. Here  $K$  and  $L$  take the values A and B and denote the type of the sites. Unlike the version of the model studied in Ref. 9, our version allows the possibility of bonding between any of the two sites which belong to two molecules of any species. The one-component version of this model with bonding allowed only between the sites of different type reduces to the S2P model considered in Ref. 9. In the case of multicomponent system with bonding allowed only between one pair of the similar type of the sites, the model reduces to the multicomponent dimerizing hard-sphere system, studied in Ref. 15.

Similar to Ref. 9 we describe this model using an orientationally averaged version of the Wertheim OZ equation, which in terms of orientationally averaged partial correlation functions  $c_{\alpha\beta}^{ab}(r)$  and  $h_{\alpha\beta}^{ab}(r)$  reads

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

where  $[\boldsymbol{\sigma}]_{ab} = \delta_{ab} \boldsymbol{\sigma}_a$  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  $\mathbf{C}(r)$ , respectively. Here  $[\mathbf{H}(r)]_{ab} = \mathbf{h}_{ab}(r)$  and  $[\mathbf{C}(r)]_{ab} = \mathbf{c}_{ab}(r)$ . In turn,  $\mathbf{h}_{ab}(r)$ ,  $\mathbf{c}_{ab}(r)$ , and  $\boldsymbol{\sigma}_a$  are the matrices which take the form

$$\mathbf{h}_{ab}(r) = \begin{pmatrix} h_{00}^{ab}(r) & h_{0A}^{ab}(r) & h_{0B}^{ab}(r) & h_{0\Gamma}^{ab}(r) \\ h_{A0}^{ab}(r) & h_{AA}^{ab}(r) & h_{AB}^{ab}(r) & h_{A\Gamma}^{ab}(r) \\ h_{B0}^{ab}(r) & h_{BA}^{ab}(r) & h_{BB}^{ab}(r) & h_{B\Gamma}^{ab}(r) \\ h_{\Gamma 0}^{ab}(r) & h_{\Gamma A}^{ab}(r) & h_{\Gamma B}^{ab}(r) & h_{\Gamma \Gamma}^{ab}(r) \end{pmatrix},$$

$$\boldsymbol{\sigma}_a = \begin{pmatrix} \sigma_{\Gamma}^a & \sigma_B^a & \sigma_A^a & \sigma_0^a \\ \sigma_B^a & 0 & \sigma_0^a & 0 \\ \sigma_A^a & \sigma_0^a & 0 & 0 \\ \sigma_0^a & 0 & 0 & 0 \end{pmatrix},$$

where the lower indices  $\alpha$  and  $\beta$  in  $\sigma_{\alpha}^a$  and in the correlation functions  $c_{\alpha\beta}^{ab}(r)$  and  $h_{\alpha\beta}^{ab}(r)$  denote the bonded states of the correspondent particle. The case of  $\alpha=0$  corresponds to unbonded particle,  $\alpha=A$  or  $\alpha=B$  to the particle with bonded site A or B, and  $\alpha=\Gamma$  to the particle with both sites, A and B, bonded. The density parameters  $\sigma_{\alpha}^a$  are related to the densities  $\rho_{\alpha}^a$  of  $\alpha$ -bonded particles by

$$\begin{aligned}\sigma_0^a &= \rho_0^a, & \sigma_A^a &= \rho_0^a + \rho_A^a, & \sigma_B^a &= \rho_0^a + \rho_B^a, \\ \sigma_\Gamma^a &= \rho_a^a = \rho_0^a + \rho_A^a + \rho_B^a + \rho_\Gamma^a.\end{aligned}\quad (3)$$

The PPY closure conditions<sup>5,9</sup> for the present model take the form

$$\begin{aligned}h_{\alpha\beta}^{ab}(r) &= -\delta_{\alpha 0}\delta_{\beta 0}, & r < R_{ab} \\ c_{\alpha\beta}^{ab}(r) &= (1-\delta_{\alpha 0})(1-\delta_{\beta 0})B_{\alpha\beta}^{ab}\delta(r-R_{ab}), & r > R_{ab}.\end{aligned}\quad (4)$$

Here the site-site potential is chosen to give the corresponding averaged Mayer function  $f_{KL}^{ab}(r)$  proportional to the Dirac  $\delta$  function

$$f_{KL}^{ab}(r) = e^{-\beta U_{KL}^{ab}(r)} - 1 = K_{KL}^{ab}\delta(r-R_{ab}), \quad (5)$$

where  $\beta = 1/k_B T$  and  $K_{KL}^{ab}$  are the stickiness parameters which are related to the constants  $B_{\alpha\beta}^{ab}$  by

$$\begin{aligned}B_{KL}^{ab} &= y_{00}^{ab}K_{KL}^{ab}, \\ B_{\Gamma A}^{ab} &= K_{AA}^{ab}y_{B0}^{ab} + K_{BA}^{ab}y_{A0}^{ab}, \\ B_{\Gamma B}^{ab} &= K_{BB}^{ab}y_{A0}^{ab} + K_{AB}^{ab}y_{B0}^{ab}, \\ B_{\Gamma\Gamma}^{ab} &= K_{AA}^{ab}y_{BB}^{ab} + K_{AB}^{ab}y_{BA}^{ab} + K_{BA}^{ab}y_{AB}^{ab} + K_{BB}^{ab}y_{AA}^{ab},\end{aligned}\quad (6)$$

and  $y_{\alpha\beta}^{ab}$  are the contact values of the cavity correlation functions defined by

$$\begin{aligned}g_{\alpha\beta}^{ab}(r) &= e^{-\beta U_{ab}^{\text{HS}}(r)}[y_{\alpha\beta}^{ab}(r) + (1-\delta_{\alpha 0})(1-\delta_{\beta 0}) \\ &\quad \times B_{\alpha\beta}^{ab}\delta(r-R_{ab})].\end{aligned}\quad (7)$$

The relation between the densities  $\rho_\alpha^a$  and parameters  $B_{\alpha\beta}^{ab}$  are found to be<sup>5,9</sup>

$$\begin{aligned}\rho_K^a &= 4\pi\rho_0^a \sum_b R_{ab}^2 [B_{KA}^{ab}(\rho_0^b + \rho_B^b) + B_{KB}^{ab}(\rho_0^b + \rho_A^b) + B_{K\Gamma}^{ab}\rho_0^b] \\ \rho_\Gamma^a &= \rho_0^a \left[ \frac{\rho_A^a \rho_B^a}{(\rho_0^a)^2} + 2\pi \sum_b \rho_0^b B_{\Gamma\Gamma}^{ab} R_{ab}^2 \right].\end{aligned}\quad (8)$$

The set of the OZ equations (2) together with the closure conditions (4) and relation between the densities (8) form a closed set of equations to be solved.

## II. SOLUTION OF THE PPY APPROXIMATION

The solution of the present PPY approximation is obtained via the Baxter factorization method.<sup>13</sup> The factorized version of the OZ equation (2) in real  $r$  space can be presented in the following form<sup>10,13-15</sup>

$$-rc_{\alpha\beta}^{ab}(r) = [q_{\alpha\beta}^{ab}(r)]' - 2\pi \sum_c \sum_{\gamma\delta} \sigma_{\gamma\delta}^c \partial/\partial r \int q_{\gamma\alpha}^{ca}(t) q_{\delta\beta}^{cb}(r+t) dt, \quad S_{ab} < r < R_{ab}, \quad (9)$$

$$-rh_{\alpha\beta}^{ab}(r) = [q_{\alpha\beta}^{ab}(r)]' - 2\pi \sum_c \sum_{\gamma\delta} \sigma_{\gamma\delta}^c \int_{S_{ac}}^{R_{ac}} q_{\alpha\gamma}^{ac}(t)(r-t)h_{\delta\beta}^{cb}(|r-t|)dt, \quad r > S_{ab}, \quad (10)$$

where  $\sigma_{\gamma\delta}^c$  is the correspondent element of the matrix  $\sigma_c$ ,  $S_{ab} = \frac{1}{2}(R_a + R_b)$  and integration in Eq. (9) with respect to  $t$  is over the range defined by  $S_{ca} < t < \min[R_{ca}, R_{cb} - r]$ .

Considering the latter of these equations in the range  $S_{ab} < r < R_{ab}$ , we finally obtain a second order polynomial for the Baxter  $q$  functions

$$q_{\alpha\beta}^{ab}(r) = (\frac{1}{2}a_\alpha^a r^2 + b_\alpha^a r)\delta_{0\beta} + c_{\alpha\beta}^{ab} \quad (11)$$

with the coefficients which follow from the boundary conditions imposed on  $q_{\alpha\beta}^{ab}(r)$

$$q_{\alpha\beta}^{ab}(R_{ab}^+) - q_{\alpha\beta}^{ab}(R_{ab}^-) = -(1-\delta_{\alpha 0})(1-\delta_{\beta 0})B_{\alpha\beta}^{ab}R_{ab} \quad (12)$$

and the following relations

$$a_\alpha^a = \delta_{\alpha 0} - 2\pi \sum_c \sum_\gamma \sigma_{\gamma 0}^c \int_{S_{ac}}^{R_{ac}} q_{\alpha\gamma}^{ac}(t)dt, \quad (13)$$

$$b_\alpha^a = 2\pi \sum_c \sum_\gamma \sigma_{\gamma 0}^c \int_{S_{ac}}^{R_{ac}} t q_{\alpha\gamma}^{ac}(t)dt. \quad (14)$$

The set of relations (12), (13), and (14) form a set of linear equations for the constants involved into  $q$ -function (11). It can be solved in much the same way as that used for

the solution of the associative PY approximation for multi-component dimerizing hard-sphere system.<sup>15</sup> After some algebra we obtain

$$\begin{aligned}a_0^a &= \frac{1}{1-\eta} + \frac{1}{2} \frac{\rho s_n R_a}{(1-\eta)^2}, \\ b_0^a &= -\frac{1}{4} \frac{\rho s_n R_a^2}{(1-\eta)^2}, \\ c_{00}^{ab} &= -\frac{R_{ab}^2}{2(1-\eta)} + \frac{1}{4} \frac{\rho s_n R_a R_{ab} S_{ab}}{(1-\eta)^2},\end{aligned}\quad (15)$$

$$a_\alpha^a = -\frac{2\pi}{1-\eta} \sum_c \sum_{\gamma \neq 0} \sigma_{\gamma 0}^c B_{\alpha\gamma}^{ac} R_{ac} R_{cc}, \quad (\alpha \neq 0),$$

$$b_\alpha^a = \frac{\pi}{1-\eta} \sum_c \sum_{\gamma \neq 0} \sigma_{\gamma 0}^c B_{\alpha\gamma}^{ac} R_{ac} R_{aa} R_{cc}, \quad (\alpha \neq 0),$$

$$c_{\alpha 0}^{ab} = \frac{\pi R_{ab} S_{ba}}{1-\eta} \sum_c \sum_{\gamma \neq 0} \sigma_{\gamma 0}^c B_{\alpha\gamma}^{ac} R_{cc} R_{ac}, \quad (\alpha \neq 0),$$

$$c_{0\alpha}^{ab} = 0, \quad (\alpha \neq 0),$$

$$c_{\alpha\beta}^{ab} = R_{ab} B_{\alpha\beta}^{ab}, \quad (\alpha \neq 0, \quad \beta \neq 0), \quad (16)$$

where  $s_n = \frac{\pi}{\rho} \sum_a \rho_a R_a^2$ ,  $\rho = \sum_a \rho_a$  and  $\eta = \frac{1}{6} \pi \sum_a \rho_a R_a^3$ .

The parameters  $B_{\alpha\beta}^{ab}$ , which enter the closure conditions (4) and the relation between the densities (8), involve the contact values of the cavity correlation functions  $y_{\alpha\beta}^{ab}(r)$ . The latter follow from Eqs. (7) and (10) considered at  $r = R_{ab}^+$

$$y_{00}^{ab}(R_{ab}) = \frac{1}{1-\eta} + \frac{1}{4} \frac{\rho s_n R_a R_b}{(1-\eta)^2 R_{ab}}, \quad (17)$$

$$\begin{aligned} R_{ab} y_{0\beta}^{ab}(R_{ab}) &= R_{ba} y_{\beta 0}^{ba}(R_{ba}) = -\frac{\pi}{1-\eta} R_{aa} \\ &\times \sum_c \sum_{\gamma \neq 0} \sigma_0^c R_{bc} R_{cc} B_{\gamma\beta}^{ch}, \quad (\beta \neq 0), \\ R_{ab} y_{\alpha\beta}^{ab}(R_{ab}) &= 2\pi \sum_c \sum_{\gamma \delta \neq 0} \sigma_\gamma^c R_{bc} R_{ac} B_{\alpha\gamma}^{ac} B_{\delta\beta}^{cb}, \\ &(\alpha \neq 0, \quad \beta \neq 0). \end{aligned} \quad (18)$$

The relations (8), (6), and (18) form a closed set of algebraic equations for the unknowns  $\rho_a^a, y_{0L}^{ab}$ , and  $y_{KL}^{ab}$ . After some algebra this set can be reduced to a set of  $2n$  linear equations for the unknowns  $Y_K^b = R_{ab}/R_{aa} y_{0K}^{ab}$

$$\begin{aligned} Y_K^a + \frac{\pi}{1-\eta} R_{aa} \sum_b R_{ab} R_{bb} [K_{KA}^{ab} Y_B^b + K_{KB}^{ab} Y_A^b] \rho_0^b \\ = -\frac{\pi}{1-\eta} \sum_b R_{ab} R_{bb} y_{00}^{ba} [(\rho_0^b + \rho_B^b) K_{AK}^{ba} \\ + (\rho_0^b + \rho_A^b) K_{BK}^{ba}] \end{aligned} \quad (19)$$

and a set of  $3n$  nonlinear algebraic equations which follows from Eq. (8)

$$\begin{aligned} \rho_K^a &= 4\pi \rho_0^a \sum_b \{y_{00}^{ab}[(\rho_0^b + \rho_B^b) K_{KA}^{ab} + (\rho_0^b + \rho_A^b) K_{KB}^{ab}] R_{ab}^2 \\ &+ R_{aa} R_{ab} [K_{KB}^{ab} Y_A^b + K_{KA}^{ab} Y_B^b] \rho_0^b\}, \\ \rho_a - \rho_A^a - \rho_B^a - \rho_0^a \\ &= \rho_0^a \left[ \frac{\rho_A^a \rho_B^a}{(\rho_0^a)^2} + 4\pi^2 \sum_{bc} \rho_0^b R_{bc} R_{ac} R_{ab}^2 y_{00}^{ac} y_{00}^{cb} K_{abc} \right], \end{aligned} \quad (20)$$

where

$$\begin{aligned} K_{abc} &= K_{AA}^{ab} [K_{BA}^{ac} K_{BB}^{cb} + K_{BB}^{ac} K_{AB}^{cb}] + K_{AB}^{ab} [K_{BA}^{ac} K_{BA}^{cb} + K_{BB}^{ac} K_{AA}^{cb}] \\ &+ K_{BA}^{ab} [K_{AA}^{ac} K_{BB}^{cb} + K_{AB}^{ac} K_{AB}^{cb}] \\ &+ K_{BB}^{ab} [K_{AA}^{ac} K_{BA}^{cb} + K_{AB}^{ac} K_{AA}^{cb}]. \end{aligned}$$

We propose an iterative method for the solution of the set of Eqs. (19) and (20). An iterative loop consists of two steps. On the first step, the solution of the set of nonlinear equations (20) is obtained for the densities  $\rho_a^a$ , which are then used as an input into the second step, in which the set of linear equations (19) is solved for the unknowns  $Y_K^a$ . As a starting point in this iterative procedure we propose to solve the following set of nonlinear equations for the densities

$$\begin{aligned} \rho_K^a &= 4\pi \rho_0^a \sum_b R_{ab}^2 \{y_{00}^{ab}[(\rho_0^b + \rho_B^b) K_{KA}^{ab} + (\rho_0^b + \rho_A^b) K_{KB}^{ab}]\}, \\ \rho_a - \rho_A^a - \rho_B^a - \rho_0^a &= \frac{\rho_A^a \rho_B^a}{\rho_0^a}, \end{aligned} \quad (21)$$

which follows from Eq. (8) if the analogue of the single bonding approximation<sup>5,9</sup>

$$B_{A\Gamma}^{ab} = 0, \quad B_{\Gamma\Gamma}^{ab} = 0$$

is used.

### III. CONCLUDING REMARKS

An analytical solution of the PPY approximation for the multicomponent totally flexible sticky two-point model of polymerizing fluid is obtained in closed form. The model is an extension of the totally flexible sticky two-point model of Wertheim to the multicomponent case. In the case of a one-component system with bonding allowed only between the sites of different type, our solution reduces to that obtained in Ref. 9 if the single bonding approximation is used. In the case of a multicomponent system with bonding allowed only between one pair of the similar type of the sites, the solution reduces to that obtained in Ref. 15 for the multicomponent dimerizing hard-sphere system. Predictions of the present PPY approximation for both of these limiting cases are in good agreement with the corresponding computer simulation results.<sup>9,15</sup> We therefore expect that it will be equally accurate for the multicomponent version of the totally flexible sticky two-point model considered here.

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