UDC 532/533,536,537.226,538.9,541.135; PACS 61.20

SOLUTION OF THE POLYMER PERCUS-YEVICK APPROXIMATION FOR THE MULTIARM STAR POLYMERIZATION

Yu.V.Kalyuzhnyi

Institute for Condensed Matter Physics of the Ukrainian National Academy of Sciences, 1 Svientsitskii St., UA–290011 Lviv, Ukraine

Received November 6, 1997

An analytical solution of the polymer Percus-Yevick approximation for a multicomponent mixture of associating hard spheres, forming star polymer molecules upon association, is derived. Simplified version of the solution, which combines the polymer Percus-Yevick approximation with the so-called ideal chain approximation is used to describe the equilibrium properties of the two-component associating mixture of hard spheres and linear chain molecules. The structure properties of the model are studied at all degrees of association, including the limit of complete association in which the system is represented by the fluid of multiarm polymer star molecules.

1. Introduction

In recent years a number of integral equation studies of the structure and thermodynamic properties of polymer fluids have been published. These include the application of the polymer reference interaction site model theory (PRISM) (see Refs. [1,2] and references therein), the polymer Born-Green-Yvon (PBGY) theory [3,4], a version of the Percus-Yevick (PY) theory extended to polymer fluids [5], a theory based on the Chandler-Silbey-Ladanyi PY approximation for the site-site fluid [6] and the multidensity polymer PY (PPY) theory for associating fluids [7,8] appropriately modified to describe polymer fluids [9–13].

However, all of these studies are focused on the investigation of the polymer fluids represented by the system of monomers that have completely associated into polymers of a fixed size, usually into linear freely-jointed chain polymers of a fixed length. More recently an analytical solution of the multidensity PPY theory was used to describe an associating fluid which polymerizes into freely-jointed tangent hard-sphere linear chain molecules [2,11]. The structure properties of such a system was studied at all the degrees of polymerization, including the limit of completely dissociated and completely associated systems.

In this paper an analytical solution of the PPY approximation, formulated for the model of the associating fluid which forms polymer star molecules upon association, is derived. We also propose a simplified version of the solution, in which the PPY approximation is supplemented by the so-called ideal chain approximation [8,9,12,13]. Solution of the PPY ideal chain approximation is utilized to study the structure properties of the associating mixture of hard spheres and linear chain molecules of a fixed length

at all the degrees of association. The model of this type can be used to describe the properties of star polymer systems, and polymer coated colloidal systems.

2. The model and theory

We consider a model represented by the $(n_p + n_c)$-component mixture of hard-sphere particles with hard spheres of each of n_p species having two sticky points, A and B, randomly placed on the surface, and hard spheres of each of n_c species having only one sticky site 0 placed in the center of the hard sphere. The pair potential $U^{ab}_{\alpha\beta}(12)$ for this model consists of the hard-sphere term and terms describing the sticky interaction

$$U^{ab}_{\alpha\beta}(12) = \phi^{ab}_{\alpha\beta}(r) + \sum_{ij} \{\delta_{ap}\delta_{bp}(1-\delta_{ij})(1-\delta_{i0})(1-\delta_{j0}) +$$

$$\delta_{ap}\delta_{bc}(1-\delta_{i0})\delta_{j0} + \delta_{ac}\delta_{bp}(1-\delta_{j0})\delta_{i0}\}\,\Phi^{ab}_{\alpha_i\beta_j}(12) \qquad (2.1)$$

where the upper indices a and b, each taking the values p or c, and together with the lower indices α and β, each taking the values $1, 2, ..., n_a$ and $1, 2, .., n_b$, stand for the species of the particles. Here $\phi^{ab}_{\alpha\beta}(r)$ is the hard-sphere potential

$$\phi^{ab}_{\alpha\beta}(r) = \begin{cases} \infty, & r < R^{ab}_{\alpha\beta} \\ 0, & r > R^{ab}_{\alpha\beta} \end{cases} \qquad (2.2)$$

$R^{ab}_{\alpha\beta} = \frac{1}{2}(R^a_\alpha + R^b_\beta)$, R^a_α is the hard-sphere diameter, δ_{ab} is the Kroneker delta, $\Phi^{ab}_{\alpha_i\beta_j}(12)$ is the site-site potential of the sticky interaction between the sites i and j belonging to the particles of (a, α) and (b, β) species, respectively, and arguments 1 and 2 denote the positions and orientations of the two particles. The summation in (2.1) is carried out over i and j taking the values $0, A, B$, and we assume that the sticky interaction is valid only between the sites of a different type. Thus, in our notation the species of each of the particles is defined by a pair of indices, (a, α), and the type of each of the attractive sites is defined by a set of three indices, (a, α, i).

Due to the short-range character of the sticky site-site interaction and due to the random location of the attractive sites, the p-type of the particles polymerizes into freely-jointed tangent hard-sphere linear chain molecules. The structure of the clusters which involve the c-type of the particles is similar to that formed by the Smith-Nezbeda primitive model of associating fluid [14,17,16], i.e. each of the p-type of the particles can simultaneously be bonded to a limited number of the c-type of the particles (in the present case not more than to two c-type particles), while the c-type of the particles can bond an arbitrary number of the p-type of the particles.

The model in question is described using a version of the multidensity integral equation theory for associating fluids which combines a four-density theory for linear chain polymerization [2,7,8,11] and a two-density theory developed to treat the systems with strong assymetry in associative interaction [14,16–18]. Similarly, as in the earlier studies, we are using an orientationally averaged multidensity Ornstein-Zernike (OZ) equation supplemented by the PPY approximation. The corresponding OZ equation,

written in terms of the orientationally averaged partial total $h^{ab}_{\alpha_i\beta_j}(r)$ and direct $c^{ab}_{\alpha_i\beta_j}(r)$ correlation functions reads

$$\hat{\mathbf{h}}^{ab}_{\alpha\beta}(k) = \hat{\mathbf{c}}^{ab}_{\alpha\beta}(k) + \sum_{d\gamma} \hat{\mathbf{c}}^{ad}_{\alpha\gamma}(k)\boldsymbol{\rho}^{(d)}_{\gamma}\hat{\mathbf{h}}^{db}_{\gamma\beta}(k) \tag{2.3}$$

where $\hat{\mathbf{h}}^{ab}_{\alpha\beta}(k)$, $\hat{\mathbf{c}}^{ab}_{\alpha\beta}(k)$ and $\boldsymbol{\rho}^{(a)}_{\alpha}$ are the matrices of the following form:

$$\hat{\mathbf{h}}^{pp}_{\alpha\beta}(k) = \begin{pmatrix} \hat{h}^{pp}_{\alpha_0\beta_0}(k) & \hat{h}^{pp}_{\alpha_0\beta_A}(k) & \hat{h}^{pp}_{\alpha_0\beta_B}(k) & \hat{h}^{pp}_{\alpha_0\beta_\Gamma}(k) \\ \hat{h}^{pp}_{\alpha_A\beta_0}(k) & \hat{h}^{pp}_{\alpha_A\beta_A}(k) & \hat{h}^{pp}_{\alpha_A\beta_B}(k) & \hat{h}^{pp}_{\alpha_A\beta_\Gamma}(k) \\ \hat{h}^{pp}_{\alpha_B\beta_0}(k) & \hat{h}^{pp}_{\alpha_B\beta_A}(k) & \hat{h}^{pp}_{\alpha_B\beta_B}(k) & \hat{h}^{pp}_{\alpha_B\beta_\Gamma}(k) \\ \hat{h}^{pp}_{\alpha_\Gamma\beta_0}(k) & \hat{h}^{pp}_{\alpha_\Gamma\beta_A}(k) & \hat{h}^{pp}_{\alpha_\Gamma\beta_B}(k) & \hat{h}^{pp}_{\alpha_\Gamma\beta_\Gamma}(k) \end{pmatrix},$$

$$\hat{\mathbf{h}}^{cp}_{\alpha\beta}(k) = \left(\hat{h}^{cp}_{\alpha_0\beta_0}(k),\ \hat{h}^{cp}_{\alpha_0\beta_A}(k),\ \hat{h}^{cp}_{\alpha_0\beta_B}(k),\ \hat{h}^{pp}_{\alpha_0\beta_\Gamma}(k)\right),\quad \hat{\mathbf{h}}^{cc}_{\alpha\beta}(k) = \hat{h}^{cc}_{\alpha_0\beta_0}(k),$$

$$\boldsymbol{\rho}^{(p)}_{\alpha} = \begin{pmatrix} \rho^p_\alpha & \rho^p_\alpha & \rho^p_\alpha & \rho^p_\alpha \\ \rho^p_\alpha & 0 & (\rho^p_\alpha)^2/\Delta^{(p)}_\alpha & 0 \\ \rho^p_\alpha & (\rho^p_\alpha)^2/\Delta^{(p)}_\alpha & 0 & 0 \\ \rho^p_\alpha & 0 & 0 & 0 \end{pmatrix}, \qquad \boldsymbol{\rho}^{(c)}_{\alpha} = \rho^{(c)}_{\alpha},$$

and

$$\Delta^{(p)}_{\alpha} = \frac{\sigma^{(p)}_{\alpha_A}\sigma^{(p)}_{\alpha_B}}{\sigma^{(p)}_{\alpha_0}}, \qquad \sigma^{(p)}_{\alpha_i} = \sum_{j=0}^{i} \rho^{(p)}_{\alpha_j}.$$

Here $\hat{h}^{ab}_{\alpha_i\beta_j}(k)$ and $\hat{c}^{ab}_{\alpha_i\beta_j}(k)$ are the Fourier transforms of the partial correlation functions $h^{ab}_{\alpha_i\beta_j}(r)$ and $c^{ab}_{\alpha_i\beta_j}(r)$, respectively, the lower indices i and j in $\rho^{(a)}_{\alpha_i}$, $\sigma^{(a)}_{\alpha_i}$ and in partial correlation functions denote the bonding states of the corresponding particle. In the case of the p-type of the particle $i = 0$ corresponds to an unbonded particle, $i = A$(or B) – to a particle bonded at A(or B) site and $i = \Gamma$ to a particle bonded at both A and B sites. Since the c-type of the particles does not have off-center attractive sites, we follow the earlier developments [14,16,18] and do not distinguish between their bonded states. In this case the index denoting the bonding states of the corresponding c-type particle is taking only one value of $i = 0$.

The PPY closure relations for the present model take the form

$$h^{ab}_{\alpha_i\beta_j}(r) = -\delta_{i0}\delta_{j0}, \qquad r < R^{ab}_{\alpha\beta}$$

$$c^{ab}_{\alpha_i\beta_j}(r) = \{\delta_{ap}\delta_{bp}(1-\delta_{ij})(1-\delta_{i0})(1-\delta_{j0}) + \delta_{ap}\delta_{bc}(1-\delta_{i0})\delta_{j0} +$$
$$\delta_{ac}\delta_{bp}(1-\delta_{j0})\delta_{i0}\}\, B^{ab}_{\alpha_i\beta_j}\delta(r - R^{ab}_{\alpha\beta}), \qquad r \geq R^{ab}_{\alpha\beta} \tag{2.4}$$

The sticky potential $\Phi^{ab}_{\alpha_i\beta_j}(12)$ is entering the closure relation (2.4) via the angle averaged Mayer function $\tilde{f}^{ab}_{\alpha_i\beta_j}(r)$ which is proportional to the Dirac delta-function

$$\tilde{f}^{ab}_{\alpha_i\beta_j}(r)\exp\left[-\beta\phi^{ab}_{\alpha\beta}(r)\right] = \{\delta_{ap}\delta_{bp}(1-\delta_{ij})(1-\delta_{i0})(1-\delta_{j0}) +$$
$$\delta_{ap}\delta_{bc}(1-\delta_{i0})\delta_{j0} + \delta_{ac}\delta_{bp}(1-\delta_{j0})\delta_{i0}\}\, K^{ab}_{\alpha_i\beta_j}\delta(r - R^{ab}_{\alpha\beta}) \tag{2.5}$$

where $K^{ab}_{\alpha_i\beta_j}$ is a stickiness parameter related to $B_{\alpha_i\beta_j}$ by

$$B^{pp}_{\alpha_K\beta_L} = \frac{1}{\rho^{(p)}_\alpha \rho^{(p)}_\beta}\chi^{pp}_{\alpha_K\beta_L} y^{pp}_{\alpha_0\beta_0}, \qquad B^{pp}_{\alpha_K\beta_\Gamma} = \frac{1}{\rho^{(p)}_\alpha \Delta^{(p)}_\beta}\sum_{L=A}^{B}\chi^{pp}_{\alpha_K\beta_L} y^{pp}_{\alpha_0\beta_{\Gamma-L}},$$

$$B^{pp}_{\alpha_\Gamma\beta_\Gamma} = \frac{1}{\Delta^{(p)}_\alpha \Delta^{(p)}_\beta}\sum_{KL=A}^{B}\chi^{pp}_{\alpha_K\beta_L} y^{pp}_{\alpha_{\Gamma-K}\beta_{\Gamma-L}},$$

$$B^{cp}_{\alpha_0\beta_L} = \frac{1}{\rho^{(p)}_\beta}\chi^{cp}_{\alpha_0\beta_L} y^{cp}_{\alpha_0\beta_0}, \qquad B^{cp}_{\alpha_0\beta_\Gamma} = \frac{1}{\Delta^{(p)}_\beta}\sum_{L=A}^{B}\chi^{cp}_{\alpha_0\beta_L} y^{cp}_{\alpha_0\beta_{\Gamma-L}} \tag{2.6}$$

where

$$\chi^{pp}_{\alpha_K\beta_L} = \sigma^{(p)}_{\alpha_{\Gamma-K}}\sigma^{(p)}_{\alpha_{\Gamma-L}} K^{pp}_{\alpha_K\beta_L}, \qquad \chi^{cp}_{\alpha_0\beta_L} = \sigma^{(p)}_{\beta_{\Gamma-L}} K^{cp}_{\alpha_0\beta_L}. \tag{2.7}$$

Subindices K and L each take the values A or B, $\Gamma - A = B$ and $y^{ab}_{\alpha_i\beta_j}$ is the contact value of the partial cavity distribution function defined by

$$g^{ab}_{\alpha_i\beta_j}(r) = e^{-\beta\phi^{ab}_{\alpha\beta}(r)}\Big\{y^{ab}_{\alpha_i\beta_j}(r) + [\delta_{ap}\delta_{bp}(1-\delta_{ij})(1-\delta_{i0})(1-\delta_{j0}) +$$

$$+\delta_{ap}\delta_{bc}(1-\delta_{i0})\delta_{j0} + \delta_{ac}\delta_{bp}(1-\delta_{j0})\delta_{i0}]\, B^{ab}_{\alpha_i\beta_j}\delta(r-R)\Big\}, \tag{2.8}$$

where $g^{ab}_{\alpha_i\beta_j}(r) = h^{ab}_{\alpha_i\beta_j}(r) - \delta_{i0}\delta_{j0}$. Finally, the relation between the densities of bonded and unbonded particles are found to be

$$\Delta^{(p)}_\alpha = 4\pi\rho^{(p)}_\alpha\left[\sum_\beta^{n_p}\rho^{(p)}_\beta (R^{pp}_{\alpha\beta})^2\left(B^{pp}_{\alpha_K\beta_A} + B^{pp}_{\alpha_K\beta_B} + B^{pp}_{\alpha_K\beta_\Gamma}\right) + \right.$$

$$\left. \sum_\beta^{n_c}\rho^{(c)}_\beta (R^{pc}_{\alpha\beta})^2 B^{pc}_{\alpha_K\beta_0}\right] + \sigma^{(p)}_{\Gamma-K}, \tag{2.9}$$

$$\rho^{(p)}_\alpha = \Delta^{(p)}_\alpha + 2\pi\rho^{(p)}_\alpha\left[\sum_\beta^{n_p}\rho^{(p)}_\beta (R^{pp}_{\alpha\beta})^2\left(B^{pp}_{\alpha_\Gamma\beta_A} + B^{pp}_{\alpha_\Gamma\beta_B} + B^{pp}_{\alpha_\Gamma\beta_\Gamma}\right) + \right.$$

$$\left. \sum_\beta^{n_c}\rho^{(c)}_\beta (R^{pc}_{\alpha\beta})^2 B^{pc}_{\alpha_\Gamma\beta_0}\right]. \tag{2.10}$$

3. General solution of the PPY approximation

The solution of the present version of the PPY approximation is obtained by using Baxter-Wertheim factorization technique. The general scheme of the solution is quite similar to that derived in [2,11], and we follow these earlier studies closely. The factorized version of the OZ equation (2.3) can be presented in the following form:

$$-rh^{ab}_{\alpha_i\beta_j}(r) = \left[q^{ab}_{\alpha_i\beta_j}(r)\right]' -$$

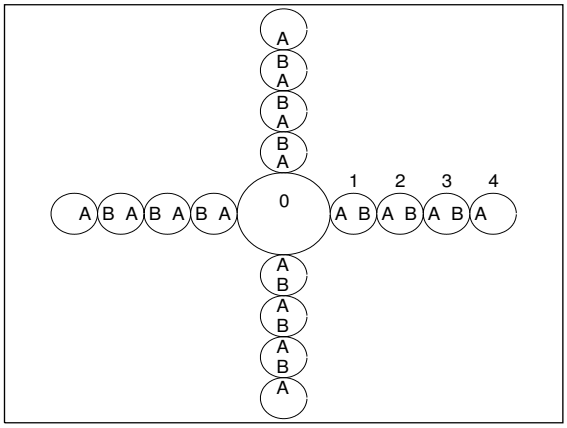

Figure 1. 4-arm molecular model, studied in Section 4, in the complete association limit. The c-type of the particles is represented by the central bead, while the rest of the beads belong to the p-type of the particles

$$2\pi\frac{\partial}{\partial r}\sum_{d}\sum_{\gamma}^{n_d}\sum_{kl}^{\Gamma_n(d)}\rho_{\gamma_{kl}}^{(d)}\int_{S_{\alpha\gamma}^{ad}}^{R_{\alpha\gamma}^{ad}}q_{\alpha_i\gamma_k}^{ad}(t)(r-t)h_{\gamma_l\beta_j}^{db}(|r-t|)\,\mathrm{t}, \qquad r > S_{\alpha\beta}^{ab} \quad (3.11)$$

$$-rc_{\alpha_i\beta_j}^{ab}(r) = \left[q_{\alpha_i\beta_j}^{ab}(r)\right]' -$$

$$2\pi\frac{\partial}{\partial r}\sum_{d}\sum_{\gamma}^{n_d}\sum_{kl}^{\Gamma_n(d)}\rho_{\gamma_{kl}}^{(d)}\int q_{\gamma_k\alpha_i}^{da}(t)q_{\gamma_l\beta_j}^{db}(r+t)\,\mathrm{t}, \qquad S_{\alpha\beta}^{ab} < r < R_{\alpha\beta}^{ab} \quad (3.12)$$

where $\rho_{\alpha_{ij}}^{(a)}$ is the correspondent elements of the matrix $\boldsymbol{\rho}_{\alpha}^{(a)}$, $\Gamma_n(a) = (1-\delta_{ac})\Gamma$, $S_{\alpha\beta}^{ab} = \frac{1}{2}(R_{\alpha}^{a} - R_{\beta}^{b})$ and integration in (3.12) is carried out over the range defined by $S_{\gamma\alpha}^{da} < t < \min[R_{\gamma\alpha}^{da}, R_{\gamma\beta}^{db} - r]$.

Considering equation (3.11) in the range $S_{\alpha\beta}^{ab} < r < R_{\alpha\beta}^{ab}$ and taking into account the closure relations (2.4) together with the boundary conditions

$$q_{\alpha_i\beta_j}^{ab}(R_{\alpha\beta}^{ab}+) - q_{\alpha_i\beta_j}^{ab}(R_{\alpha\beta}^{ab}-) = -\left[\delta_{ap}\delta_{bp}(1-\delta_{ij})(1-\delta_{i0})(1-\delta_{j0}) + \right.$$

$$\left.\delta_{ap}\delta_{bc}(1-\delta_{i0})\delta_{j0} + \delta_{ac}\delta_{bp}(1-\delta_{j0})\delta_{i0}\right] R_{\alpha\beta}^{ab}B_{\alpha_i\beta_j}^{ab} \quad (3.13)$$

we finally obtain

$$q_{\alpha_i\beta_j}^{ab}(r) = \left(\frac{1}{2}a_{\alpha_i}^{a}r^2 + b_{\alpha_i}^{a}r\right)\delta_{0j} + d_{\alpha_i\beta_j}^{ab} \quad (3.14)$$

where

$$a_{\alpha_0}^{a} = \frac{1}{1-\eta} + \frac{\rho s_n R_{\alpha}^{a}}{2(1-\eta)^2} - \frac{2\pi}{1-\eta}\delta_{ac}\sum_{\gamma}^{n_p}\rho_{\gamma}^{(p)}R_{\gamma}^{p}R_{\alpha\gamma}^{cp}\sum_{j\neq 0}^{\Gamma}B_{\alpha_0\gamma_j}^{cp}, \quad (3.15)$$

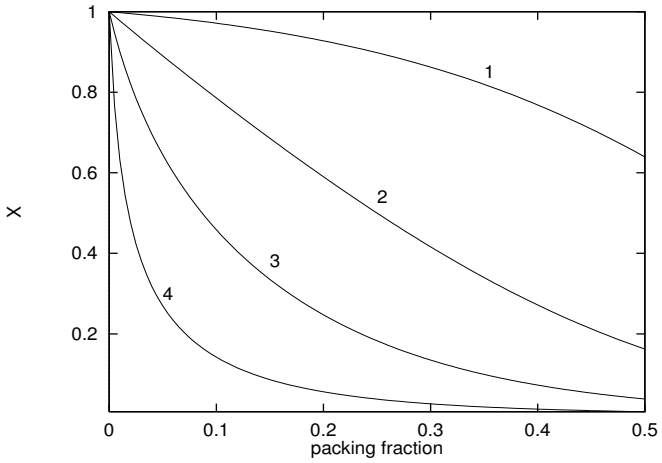

Figure 2. Fraction of unbonded chain molecules $x = \sigma_{1_B}^{(p)}/\rho^{(p)}$ as a function of the total packing fraction of the system η at (1) $K_{pc} = 0.1$, (2) $K_{pc} = 1$, (3) $K_{pc} = 5$, (4) $K_{pc} = 30$.

$$b^a_{\alpha_0} = -\frac{1}{4}\frac{\rho s_n (R^a_\alpha)^2}{(1-\eta)^2} + \frac{\pi R^c_\alpha}{1-\eta}\delta_{ac}\sum_\gamma^{n_p}\rho^{(p)}_\gamma R^p_\gamma R^{cp}_{\alpha\gamma}\sum_{j\neq 0}^{\Gamma} B^{cp}_{\alpha_0\gamma_j}, \tag{3.16}$$

$$d^{ab}_{\alpha_0\beta_0} = -\frac{(R^{ab}_{\alpha\beta})^2}{2(1-\eta)} + \frac{1}{4}\frac{\rho s_n R^a_\alpha R^{ab}_{\alpha\beta} S^{ab}_{\alpha\beta}}{(1-\eta)^2} + \frac{\pi}{1-\eta} R^{cb}_{\alpha\beta} S^{bc}_{\beta\alpha}\delta_{ac}\sum_\gamma^{n_p}\rho^{(p)}_\gamma R^p_\gamma R^{cp}_{\alpha\gamma}\sum_{j\neq 0}^{\Gamma} B^{cp}_{\alpha_0\gamma_j}, \tag{3.17}$$

$$a^p_{\alpha_i} = -\frac{2\pi}{1-\eta}\sum_\gamma^{n_p}\rho^{(p)}_\gamma R^p_\gamma R^{pp}_{\alpha\gamma}\sum_{j\neq 0}^{\Gamma} B^{pp}_{\alpha_i\gamma_j} + \sum_\gamma^{n_c}\rho^{(c)}_\gamma R^c_\gamma R^{pc}_{\alpha\gamma} B^{pc}_{\alpha_i\gamma_0}, \quad (i\neq 0) \tag{3.18}$$

$$b^p_{\alpha_i} = -\frac{1}{2} R^p_\alpha a^a_{\alpha_i}, \quad (i\neq 0) \tag{3.19}$$

$$d^{pb}_{\alpha_i\beta_0} = -\frac{1}{2} R^{pb}_{\alpha\beta} S^{bp}_{\beta\alpha} a^a_{\alpha_i} + \delta_{bc} R^{pc}_{\alpha\beta} B^{pc}_{\alpha_i\beta_0}, \quad (i\neq 0) \tag{3.20}$$

$$d^{ab}_{\alpha_i\beta_j} = \left[(1-\delta_{i0})\delta_{ap} + \delta_{ac}\right] R^{ab}_{\alpha\beta} B^{ab}_{\alpha_i\beta_j}, \quad (j\neq 0) \tag{3.21}$$

and we use the following notation

$$\rho = \sum_a\sum_\alpha^{n_a}\rho^{(a)}_\alpha, \qquad s_n = \frac{\pi}{\rho}\sum_a\sum_\alpha^{n_a}\rho^{(a)}_\alpha (R^a_\alpha)^2, \qquad \eta = \frac{\pi}{6}\sum_a\sum_\alpha^{n_a}\rho^{(a)}_\alpha (R^a_\alpha)^3$$

The contact values of the cavity distribution function follow from equation (3.11) considered at $r \to R^{ab}_{\alpha\beta}$

$$R^{ab}_{\alpha\beta} y^{ab}_{\alpha_0\beta_0}(R^{ab}_{\alpha\beta}+) = \frac{1}{1-\eta} + \frac{1}{4}\frac{\rho s_n R^a_\alpha R^b_\beta}{(1-\eta)^2 R^{ab}_{\alpha\beta}} -$$

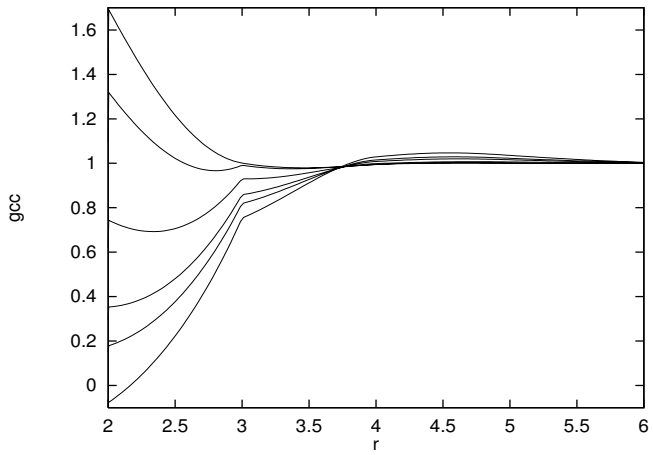

Figure 3. Radial distribution function $g_{cc}(r)$ at $\eta = 0.1$ and different values of the strength of association. From the top to the bottom at $r = 2$ $K_{pc} = 0, 1, 5, 15, 30, \infty$.

$$\frac{\pi}{1-\eta}\left[\delta_{ac}R^b_\beta \sum_\gamma^{n_p} \rho^{(p)}_\gamma R^p_\gamma R^{cp}_{\alpha\gamma} \sum_{j\neq 0}^{\Gamma} B^{cp}_{\alpha_0\gamma_j} + \delta_{bc}R^a_\alpha \sum_\gamma^{n_p} \rho^{(p)}_\gamma R^p_\gamma R^{pc}_{\gamma\beta} \sum_{j\neq 0}^{\Gamma} B^{pc}_{\gamma_j\beta_0}\right] +$$

$$2\pi\delta_{ac}\delta_{bc} \sum_\gamma^{n_p} R^{cp}_{\alpha\gamma} R^{pc}_{\gamma\beta} \sum_{kl\neq 0}^{\Gamma} B^{cp}_{\alpha_0\gamma_k} \rho^{(p)}_{\gamma_{kl}} B^{pc}_{\gamma_l\beta_0}, \tag{3.22}$$

$$R^{ap}_{\alpha\beta} y^{ap}_{\alpha_0\beta_j}(R^{ap}_{\alpha\beta}+) = \frac{\pi}{\eta-1} R^a_\alpha \sum_d \sum_\gamma^{n_d} \rho^{(d)}_\gamma R^{pd}_{\beta\gamma} R^d_\gamma \sum_{l=0}^{\Gamma_n(d)} B^{dp}_{\gamma_l\beta_j} +$$

$$2\pi\delta_{ac} \sum_\gamma^{n_p} \sum_{lk\neq 0}^{\Gamma} \rho^{(p)}_{\gamma_{kl}} R^{pp}_{\beta\gamma} R^{cp}_{\alpha\gamma} B^{cp}_{\alpha_0\gamma_k} B^{pp}_{\gamma_l\beta_j}, \quad (j \neq 0) \tag{3.23}$$

$$R^{pp}_{\alpha\beta} y^{pp}_{\alpha_0\beta_j}(R^{pp}_{\alpha\beta}+) = 2\pi \sum_\gamma^{n_c} \rho^{(c)}_\gamma R^{pc}_{\alpha\gamma} R^{pc}_{\beta\gamma} B^{pc}_{\alpha_i\gamma_0} B^{cp}_{\gamma_0\beta_j} +$$

$$2\pi \sum_\gamma^{n_p} \sum_{kl\neq 0}^{\Gamma} \rho^{(p)}_{\gamma_{kl}} R^{pp}_{\beta\gamma} B^{pp}_{\alpha_i\gamma_k} B^{pp}_{\gamma_l\beta_j} R^{pp}_{\alpha\gamma} \qquad (i,j \neq 0) \tag{3.24}$$

Thus, solution of the OZ equation (2.3) closed by the PPY closure conditions (2.4) reduces to the solution of a set of algebraic equations formed by relations (2.9), (2.10) and (2.6).

4. Solution of the PPY ideal chain approximation for a two-component associative polymer-colloidal mixture

The model discussed in two previous sections is quite general and can be used to describe a number of different associating macromolecular systems. One of such systems is represented by a two-component associating mixture of chain molecules and hard spheres, which form star polymer molecules

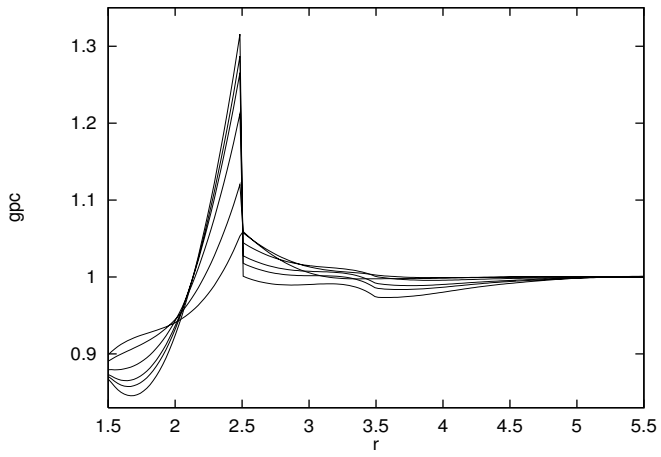

Figure 4. Average radial distribution function $g_{pc}(r)$ at $\eta = 0.1$ and different values of the strength of association. From the top to the bottom at $r = 1.5$ $K_{pc} = 0, 1, 5, 15, 30, \infty$.

upon association. This particular version of the model discussed earlier can be obtained by imposing certain restrictions on the bonding possibilities of the system. The model of this type can be used to describe such systems as polymer coated colloids and star polymer systems. In this section we will illustrate the solution of the PPY approximation, derived in the previous section, by its application to such associating polymer-colloidal systems. In addition, we will simplify the solution by utilizing the version of the so-called ideal chain approximation [8,9] proposed recently [13].

Let us consider the (n_p+1)-component version of the model with $\rho_\alpha^{(p)} = \rho^{(p)}$ and with the following conditions imposed on the values of the stickeness parameter $K^{ab}_{\alpha_i\beta_j}$

$$K^{pp}_{\alpha_K\beta_L} = K_{pp}\left(\delta_{KB}\delta_{LA}\delta_{\alpha,\beta-1} + \delta_{KA}\delta_{LB}\delta_{\alpha-1,\beta}\right)$$

$$K^{pc}_{\alpha_K 1_0} = K_{pc}\delta_{KA}\delta_{\alpha 1} \tag{4.25}$$

and restrict our study to the case of an infinitely strong sticky attraction between the p-type of the particles, i.e. $K_{pp} \to \infty$. In this limit the system is represented by a two-component mixture of hard spheres and linear chain molecules which, due to the association between the p-type and the c-type of the particles form star polymer molecules of the type shown in figure 1.

In the complete association limit ($K_{pc} \to \infty$) the average number of arms $n_{\rm arm}$ per each molecule is defined by the ratio $n_{arm} = \rho^{(p)}/\rho^{(c)}$.

For the sake of simplicity we shall describe the present model using the ideal chain approximation [8,9,12,13] which neglects the correlations between two particles with at least one of them bonded at two sites, A and B, i.e. $h^{pp}_{\alpha_i\beta_\Gamma}(r) = c^{pp}_{\alpha_i\beta_\Gamma}(r) = 0$. Thus, in the limit of $K_{pp} \to \infty$ equation (2.10) gives

$$\Delta^{(p)}_\alpha = \rho^{(p)}. \tag{4.26}$$

Substituting this result into equation (2.9) we have

$$\rho^{(p)} = 4\pi\rho^{(p)}\left\{\delta_{KB}\rho^{(p)}(R^{pp}_{\alpha,\alpha+1})^2 B^{pp}_{\alpha_B(\alpha+1)_A} +\right.$$

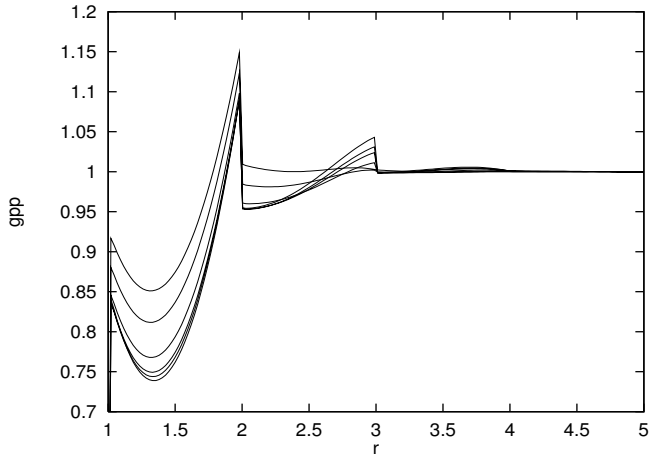

Figure 5. Average radial distribution function $g_{pp}(r)$ at $\eta = 0.1$ and different values of the strength of association. From the top to the bottom at $r = 1.4$ $K_{pc} = 0, 1, 5, 15, 30, \infty$.

$$\delta_{KA}\left[\rho^{(p)}(R^{pp}_{\alpha,\alpha-1})^2 B^{pp}_{\alpha_A(\alpha-1)_B} + \rho^{(c)}\delta_{\alpha 1}(R^{pc}_{11})^2 B^{pc}_{1_A 1_0}\right]\Big\} + \sigma^{(p)}_{\alpha_\Gamma - K}. \tag{4.27}$$

In the complete association limit ($K_{pp} \to \infty$) $\sigma^{(p)}_{\alpha_K} = 0$ for all values of α and K, except $\alpha = 1$ and $K = B$. Thus,

$$B^{pp}_{\alpha_K \beta_L} = \frac{1}{4\pi\rho^{(p)}}\left[\delta_{KB}\delta_{LA}\frac{\delta_{\alpha,\beta-1}}{(R^{pp}_{\alpha,\alpha+1})^2} + \delta_{KA}\delta_{LB}\frac{\delta_{\alpha,\beta+1}}{(R^{pp}_{\alpha,\alpha-1})^2}\right] \tag{4.28}$$

$$B^{pc}_{1_A 1_0} = \frac{\rho^{(p)} - \sigma^{(p)}_{1_B}}{4\pi\rho^{(p)}\rho^{(c)}(R^{pc}_{11})^2} \tag{4.29}$$

The corresponding relation between the strength of the sticky interaction K_{pc} and density parameter $\sigma^{(p)}_{1_B}$ follows from (4.29)

$$\frac{\pi}{1-\eta}(R^p_1)^2 K_{pc}(\sigma^{(p)}_{1_B})^2 +$$

$$\left[4\pi\rho^{(c)}(R^{pc}_{11})^2\tilde{g}^{pc}_{11}K_{pc} - \frac{\pi}{1-\eta}\rho^{(p)}(R^p_1)^2 K_{pc} + 1\right]\sigma^{(p)}_{1_B} - \rho^{(p)} = 0 \tag{4.30}$$

where expression (2.6) for $B^{pc}_{1_A 1_0}$ has been used. Here $\tilde{g}^{ab}_{\alpha\beta}$ is the hard-sphere contact value of the pair distribution function

$$\tilde{g}^{ab}_{\alpha\beta} = \frac{1}{1-\eta} + \frac{1}{4}\frac{\rho s_n R^a_\alpha R^b_\beta}{(1-\eta)^2 R^{ab}_{\alpha\beta}}$$

and in order to eliminate $y^{pc}_{1_0 1_0}$ appearing in expression (2.6) for $B^{pc}_{1_A 1_0}$ equation (3.22) has been used.

Now we are in a position to write the closed form expressions for the coefficients of the Baxter q-function and for the contact values of the partial

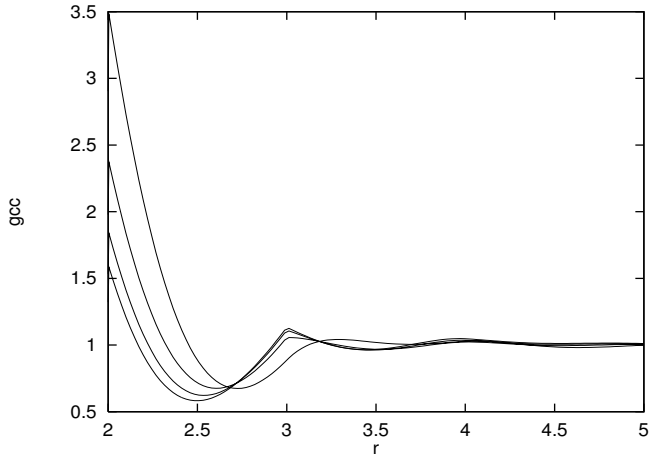

Figure 6. Radial distribution function $g_{cc}(r)$ at $\eta = 0.3$ and different values of the strength of association. From the top to the bottom at $r = 2$ $K_{pc} = 0, 1, 5, \infty$.

cavity distribution functions. Substituting (4.28) and (4.29) into (3.15)-(3.21) we obtain

$$a^{(a)}_{\alpha_0} = \frac{1}{1-\eta} + \frac{\rho s_n R^a_\alpha}{2(1-\eta)^2} - \frac{2\pi}{1-\eta}\delta_{ac}\rho^{(p)} R^p_1 R^{cp}_{11} B^{cp}_{1_0 1_A}, \tag{4.31}$$

$$b^{(a)}_{\alpha_0} = -\frac{1}{4}\frac{\rho s_n (R^a_\alpha)^2}{(1-\eta)^2} + \frac{\pi}{1-\eta} R^c_1 \delta_{ac}\rho^{(p)} R^p_1 R^{cp}_{11} B^{cp}_{1_0 1_A}, \tag{4.32}$$

$$d_{\alpha_0\beta_0} = \frac{(R^{ab}_{\alpha\beta})^2}{2(\eta-1)} + \frac{1}{4}\frac{s_n \rho R^a_\alpha R^{ab}_{\alpha\beta} S^{ab}_{\alpha\beta}}{(1-\eta)^2} + \frac{\pi}{1-\eta} R^{cb}_{1\beta} S^{bc}_{\beta 1}\delta_{ac}\rho^{(p)} R^p_1 R^{cp}_{11} B^{cp}_{1_0 1_A}, \tag{4.33}$$

$$a^{(p)}_{\alpha_K} = \frac{1}{2(1-\eta)}\left\{\delta_{AK}\left[(1-\delta_{\alpha 1})\frac{R^p_{\alpha-1}}{R^{pp}_{\alpha,\alpha-1}}\delta_{\alpha 1}\frac{\rho^{(p)} - \sigma^{(p)}_{1_B}}{\rho^{(p)}}\right] + \delta_{BK}(1-\delta_{\alpha n_p})\frac{R^p_{\alpha+1}}{R^{pp}_{\alpha,\alpha+1}}\right\}, \tag{4.34}$$

$$b^{(p)}_{\alpha_K} = -\frac{1}{2} R^p_\alpha a^{(p)}_{\alpha_K}, \tag{4.35}$$

$$d^{pb}_{\alpha_K\beta_0} = -\frac{1}{2} R^{pb}_{\alpha\beta} S^{bp}_{\beta\alpha} a^{(p)}_{\alpha_K} + \delta_{bc}\delta_{KA}\delta_{\alpha 1}\frac{\rho^{(p)} - \sigma^{(p)}_{1_B}}{4\pi\rho^{(p)}\rho^{(c)} R^{pc}_{11}}, \tag{4.36}$$

$$d^{cp}_{1_0\beta_L} = \delta_{\beta 1}\delta_{LA}\frac{\rho^{(p)} - \sigma^{(p)}_{1_B}}{4\pi\rho^{(p)}\rho^{(c)} R^{pc}_{11}}, \tag{4.37}$$

$$d^{pp}_{\alpha_K\beta_L} = \frac{1}{4\pi\rho^{(p)}}\left[\delta_{KB}\delta_{LA}\frac{\delta_{\alpha,\beta-1}}{R^{pp}_{\alpha,\alpha+1}} + \delta_{KA}\delta_{LB}\frac{\delta_{\alpha,\beta+1}}{R^{pp}_{\alpha,\alpha-1}}\right], \tag{4.38}$$

$$d^{pp}_{\alpha_0\beta_K} = 0, \tag{4.39}$$

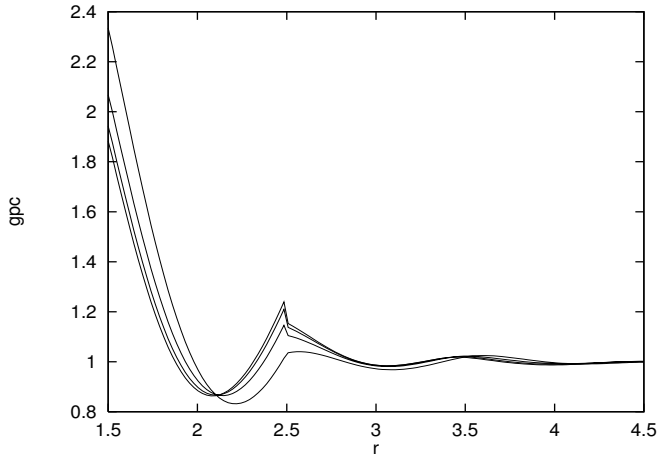

Figure 7. Average radial distribution function $g_{pc}(r)$ at $\eta = 0.3$ and different values of the strength of association. From the top to the bottom at $r = 1.5$ $K_{pc} = 0, 1, 5, \infty$.

and

$$R^{ab}_{\alpha\beta} y^{ab}_{\alpha_0\beta_0}(R^{ab}_{\alpha\beta}+) = R^{ab}_{\alpha\beta}\tilde{g}^{ab}_{\alpha\beta} - \frac{(\rho^{(p)} - \sigma^{(p)}_{1_B})}{4(1-\eta)\rho^{(c)}} \frac{R^p_1}{R^{pc}_{11}} \left(\delta_{ac} R^b_\beta + \delta_{bc} R^a_\alpha\right), \quad (4.40)$$

$$R^{ap}_{\alpha\beta} y^{ap}_{\alpha_0\beta_L}(R^{ap}_{\alpha\beta}+) = \frac{\delta_{ac}\delta_{AL}\delta_{\beta 2}}{8\pi\rho^{(p)}\rho^{(c)}} \frac{(\rho^{(p)} - \sigma^{(p)}_{1_B})}{R^{pp}_{12} R^{pc}_{11}} +$$

$$\frac{R^a_\alpha}{4(\eta-1)} \left[\delta_{LB}(1-\delta_{\beta n_p}) \frac{R^p_{\beta+1}}{R^{pp}_{\beta,\beta+1}} + \delta_{LA}(1-\delta_{\beta 1}) \frac{R^p_{\beta-1}}{R^{pp}_{\beta-1,\beta}}\right], \quad (4.41)$$

$$R^{pp}_{\alpha\beta} y^{pp}_{\alpha_K\beta_L}(R^{pp}_{\alpha\beta}+) = \delta_{\beta 1}\delta_{\alpha 1}\delta_{KA}\delta_{LA} \frac{(\rho^{(p)} - \sigma^{(p)}_{1_B})^2}{8\pi(\rho^{(p)})^2\rho^{(c)}(R^{pc}_{11})^2} +$$

$$\frac{1}{8\pi\rho^{(p)}} \left[\frac{\delta_{KB}\delta_{LA}\delta_{\alpha,\beta-2}}{R^{pp}_{\alpha,\alpha+1} R_{\alpha+1,\alpha+2}} + \frac{\delta_{KA}\delta_{LB}\delta_{\alpha,\beta+2}}{R^{pp}_{\alpha,\alpha-1} R^{pp}_{\alpha-1,\alpha-2}}\right]. \quad (4.42)$$

The set of expressions (4.31)-(4.39) together with the quadratic equation (4.30) for the density parameter $\sigma^{(p)}_{1_B}$ represents our solution of the PPY ideal chain approximation for the two-component associating polymer-colloidal mixture. Knowing the Baxter q-function (3.14) allows one to study the structure and thermodynamical properties of the model in question. The partial total pair correlation functions $h^{ab}_{\alpha_i\beta_j}(r)$ can be calculated by using the factorized version of the OZ equation (3.11) and (3.12), written in the Fourier k-space [19–21]

$$\boldsymbol{\rho}^{-1} - \hat{\mathbf{c}}(k) = \mathbf{Q}^T(-k)\boldsymbol{\rho}\mathbf{Q}(k), \quad (4.43)$$

$$\mathbf{1} + \boldsymbol{\rho}\hat{\mathbf{h}}(k) = \left[\boldsymbol{\rho}\mathbf{Q}^T(-k)\boldsymbol{\rho}\mathbf{Q}(k)\right]^{-1} \quad (4.44)$$

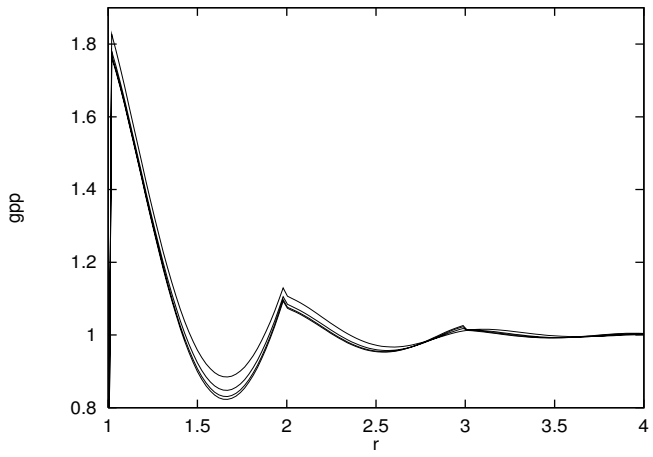

Figure 8. Average radial distribution function $g_{pp}(r)$ at $\eta = 0.3$ and different values of the strength of association. From the top to the bottom at $r = 1.7$ $K_{pc} = 0, 1, 5, \infty$.

and the expression for the Baxter q-function derived in the previous section. Here the elements of the matrices $\hat{\mathbf{h}}(k)$, $\hat{\mathbf{c}}(k)$, $\boldsymbol{\rho}$, $\mathbf{Q}(k)$ are the matrices $\hat{\mathbf{h}}^{ab}_{\alpha\beta}(k)$, $\hat{\mathbf{c}}^{ab}_{\alpha\beta}(k)$, $\delta_{\alpha\beta}\delta_{ab}\boldsymbol{\rho}^{(a)}_{\alpha}$ and $\mathbf{Q}^{ab}_{\alpha\beta}(k)$, respectively,

$$4\pi^2 q^{ab}_{\alpha_i\beta_j}(r) = \int_{-\infty}^{\infty} \left\{ \left[\boldsymbol{\rho}^{-1}\right]^{ab}_{\alpha_i\beta_j} - Q^{ab}_{\alpha_i\beta_j}(k) \right\} \exp(-ikr)\, \mathrm{k}, \tag{4.45}$$

and $\mathbf{Q}^T(k)$ denotes a matrix transposed to the matrix $\mathbf{Q}(k)$. Since in the PPY approximation $\mathbf{c}^{ab}_{\alpha\beta}(r) = 0$ for $r > R^{ab}_{\alpha\beta}$, we have

$$\mathbf{h}(r) = \frac{1}{2\pi^2 r} \int_0^{\infty} \left\{ \left[\boldsymbol{\rho}\mathbf{Q}^T(-k)\boldsymbol{\rho}\mathbf{Q}(k)\boldsymbol{\rho}\right]^{-1} + \right.$$

$$\left. \mathbf{Q}^T(-k)\boldsymbol{\rho}\mathbf{Q}(k) - 2\boldsymbol{\rho}^{-1} \right\} k \sin(kr)\, \mathrm{k} \tag{4.46}$$

5. Results and discussion

The equilibrium properties of the model at hand are defined by the total packing fraction η, the strength of associative interaction K_{pp}, the number of p-type particles species n_p (which is the length of the chain molecules), the ratio between the densities of the p-type and c-type of the particles $n_{\mathrm{arm}} = \rho^{(p)}/\rho^{(c)}$ (which is the average number of arms per each star molecule formed in the complete association limit, $K_{pc} \to \infty$). Results presented in this section apply to the version of the model with $n_{\mathrm{arm}} = 4$, $n_p = 4$, $R^p_\alpha = R_p = 1$ and $R^c_1 = R_c = 2$.

First we discuss the dependence of the fraction of free (not bonded to the c-type of the particles) chain molecules $x = \sigma^{(p)}_{1_B}/\rho^{(p)}$ on the strength of the sticky interaction K_{pc} and packing fraction η. Fig. 2 shows x as a function of the system packing fraction η for several values of the stickiness.

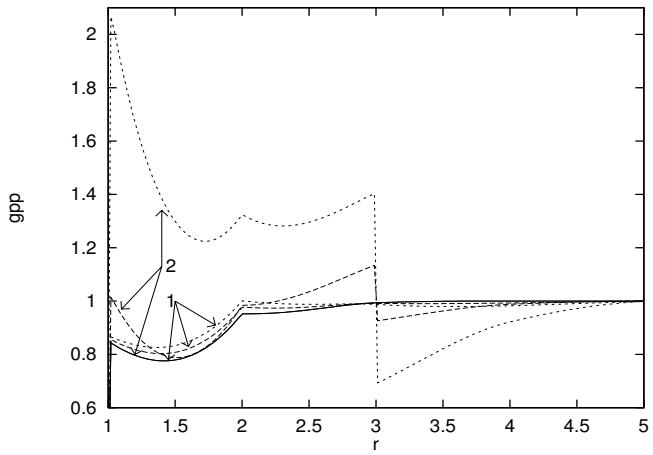

Figure 9. Radial distribution function $g_{14}^{pp}(r)$ (1) and $g_{11}^{pp}(r)$ (2) at $\eta = 0.1$ and $K_{pc} = 0$ (solid line), $K_{pc} = 5$ (long dashed line) and $K_{pc} = \infty$ (short dashed line).

As one would expect, with the increase of η and/or K_{pc} the fraction of the free chains decreases.

The version of the ideal chain approximation utilized in the present study allows one to calculate the individual radial distribution functions (RDF)

$$g_{\alpha\beta}^{ab}(r) = \sum_{ij}^{n_a n_b} g_{\alpha_i\beta_j}^{ab}(r) \tag{5.47}$$

for each of the monomer pair. In addition to these RDFs, for the description of the structure of the polymer system, the so-called averaged RDFs, are often used. For the model in question they are defined as

$$g_{pp}(r) = \frac{1}{(n_p)^2} \sum_{\alpha\beta=1}^{n_p} g_{\alpha\beta}^{pp}(r),$$

$$g_{pc}(r) = \frac{1}{n_p} \sum_{\alpha}^{n_p} g_{\alpha 1}^{pc}(r). \tag{5.48}$$

In figures 3-10 we present various RDFs for a partially associated system at two values of the total packing fraction $\eta = 0.1, 0.3$ and different values of the strength of association. From these figures one can see the changes in the structure with the increase of the degree of association from a nonassociating mixture of hard spheres and chain molecules (K_{pc}=0) to complete the association limit, $K_{pc} = \infty$, represented by the system of polymer star molecules with the average number of arms $n_{\rm arm} = 4$.

The structure peculiarities of the nonassociating mixture of hard spheres and chain molecules were discussed earlier [10]. In brief, the RDF $g_{pp}(r)$ has a jump discontinuity at $r = 2R_p$ which is the result of intramolecular correlations, while the shape of the RDF $g_{cc}(r)$ is quite similar to the RDF of the regular hard-sphere mixture. Similarly, as in the case of the site-site molecular fluids [22], the RDF $g_{pc}(r)$ has a cusp at $r = \frac{1}{2}R_c + \frac{3}{2}R_p$

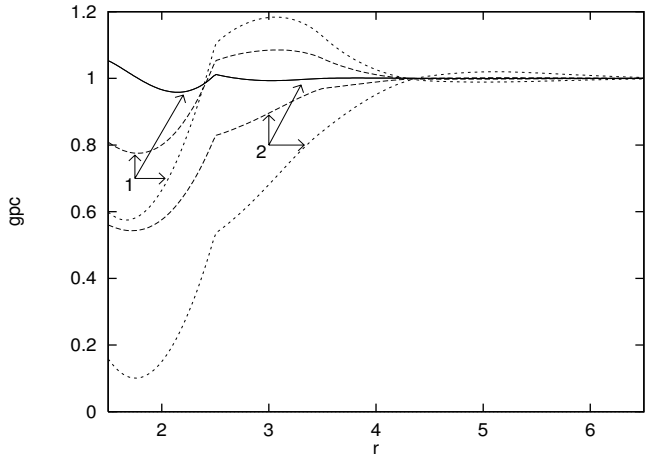

Figure 10. Radial distribution function $g_{41}^{pc}(r)$ (1) and $g_{11}^{pc}(r)$ (2) at $\eta = 0.1$ and $K_{pc} = 0$ (solid line), $K_{pc} = 5$ (long dashed line) and $K_{pc} = \infty$ (short dashed line).

(figures 4, 7). With the increase of K_{pc} the cusp of the same origin appeares on the RDF $g_{cc}(r)$ at $r = R_p + R_c$ (figures 3, 6). In addition, the RDFs $g_{pp}(r)$ and $g_{pc}(r)$ show a jump discontinuity at $r = R_p + R_c$ and $r = \frac{3}{2}R_p + \frac{1}{2}R_c$, respectively, reflecting the formation of star molecules (figures 4, 5, 7, 8). The contact values of all the three average RDFs $g_{cc}(r)$, $g_{pc}(r)$ and $g_{pp}(r)$ change their values from a value larger than 1 to a value smaller than 1 at lower values of the packing fraction ($\eta = 0.1$) (figures 3-5). The corresponding changes at higher values of the packing fraction ($\eta = 0.3$) are not so pronounced and are relatively smaller, although the association causes a decrease of the contact values of the RDF. These changes in the contact values result from the screening effects due to the adjacent bonded spheres. In figure 9 we compare the behaviour of the individual RDFs $g_{11}^{pp}(r)$ and $g_{14}^{pp}(r)$. At $K_{pc} = 0$ both RDFs coincide, while with the increase of K_{pc} they show a substantial difference. At large values of K_{pc} the RDF $g_{11}^{pp}(r)$ has a relatively large contact value, and for $r = R_c + R_p$ shows a jump discontinuity. The corresponding RDF $g_{14}^{pp}(r)$ remains almost unchanged. Similar comparison for the RDFs $g_{11}^{pc}(r)$ and $g_{41}^{pc}(r)$ is demonstrated in figure 10. Here both functions change their shapes due to the association. With the increase of K_{pc} the contact values of the RDFs $g_{11}^{pc}(r)$ and $g_{41}^{pc}(r)$ decrease as well.

6. Concluding remarks

In the present paper an analytical solution of the polymer Percus-Yevick (PPY) approximation for the multicomponent mixture of associating hard spheres, forming polymer star molecules upon association, is derived. A simplified version of the solution, which involves in addition the so-called ideal chain approximation, has been used to study the structure properties of the two-component associating mixture of hard spheres and linear chain molecules. The accuracy of the present theory has been assessed only in the complete dissociation limit ($K_{pc} = 0$) [10], since simulation results for

a partially and completely associated system are not available. We expect it to be of the same order of accuracy for all the degrees of association, but this remains to be tested. The corresponding work is in progress and its results will be reported in due cource.

Acknowledgements

This work was supported by the joint INTAS-Ukraine Call'95 grant (INTAS-UA95-133).

References

[1] Schweizer K.S., Curro J.G. PRISM theory of the structure, thermodynamics, and phase transitions of polymer liquids and alloys. In: Advances in Polymer Science, ed. L.Monnerie, U.W.Suter, Spring-Verlag Berlin Heidelberg, 1994, vol. 116, p. 320-377.

[2] Kalyuzhnyi Yu.V., Cummings P.T. Solution of the polymer Percus-Yevick approximation for the multicomponent totally flexible sticky two-point model of polymerizing fluid. // J. Chem. Phys., 1995, vol. 103, No 8, p. 3265-3267.

[3] Taylor M.P., Lipson J.E.G. A Born-Green-Yvon equation for flexible chain-molecule fluids. I. General formalism and numerical results for short hard-sphere chains. // J. Chem. Phys., 1995, vol. 102, No 5, p. 2118-2125.

[4] Attard P. Polymer Born-Green-Yvon equation with proper triplet superposition approximation. Results for hard-sphere chains. // J. Chem. Phys., 1995, vol. 102, No 13, p. 5411-5426.

[5] Chiew Y.C. Percus-Yevick integral-equation theory for athermal hard-sphere chains. Part I: Equation of state. // Mol. Phys., 1990, vol. 70, No 1, p. 129-143.

[6] Kalyuzhnyi Yu.V., Cummings P.T. Solution of the Candler-Silbey-Ladanyi equation for the multicomponent hard-sphere site-site molecular fluid: Percus-Yevick approximation. // J. Chem. Phys., 1996, vol. 105, No 5, p. 2011-2019.

[7] Wertheim M. Fluids with highly directional attractive forces. III. Multipole attraction sites. // J. Stat. Phys., 1986, vol. 42, No 3/4, p. 459-476.

[8] Wertheim M. Fluids with highly directional attractive forces. IV. Equilibrium polymerization. // J. Stat. Phys., 1986, vol. 42, No 3/4, p. 477-492.

[9] Chang J., Sandler S.I. The correlation functions of hard-sphere chain fluids: Comparison of the Wertheim integral equation theory with the Monte Carlo simulation. // J. Chem. Phys., 1995, vol. 102, No 1, p. 437-449.

[10] Chang J., Sandler S.I. The Wertheim integral equation theory with the ideal chain approximation and a dimer equation of state: Generalization to mixtures of hard-sphere chain fluids. // J. Chem. Phys., 1995, vol. 103, No 8, p. 3196-3211.

[11] Kalyuzhnyi Yu.V., Lin C.-T., Stell G. Primitive models of chemical association. II. Polymerization into flexible chain molecules of prescribed length. // J. Chem. Phys., 1997, vol. 106, No 4, p. 1940-1949.

[12] Kalyuzhnyi Yu.V. Polymer Percus-Yevick ideal chain approximation for the Lennard-Jones chain fluid. // Cond. Matt. Phys., 1997, No 10, p. 51-60.

[13] Kalyuzhnyi Yu.V., Lin C.-T., Stell G. Polymer Percus-Yevick ideal chain approximation for the mixture of heteronuclear hard-sphere chain fluid. // J. Chem. Phys., 1997, (submitted).

[14] Wertheim M.S. Integral equation for the Smith-Nezbeda model of associated fluids. // J. Chem. Phys., 1988, vol. 88, No 11, p. 1145-1155.

[15] Holovko M.F., Kalyuzhnyi Yu.V. On the effects of association in the statistical theory of ionic systems. Analytic solution of the PY-MSA version of the Wertheim theory. // Mol. Phys., 1991, vol. 73, No 5, p. 1145-1157.

[16] Kalyuzhnyi Yu.V., Vlachy V. Integral equation theory for highly asymmetric electrolyte solution. // Chem. Phys. Lett., 1993, vol. 215, No 5, p. 518-522.

[17] Kalyuzhnyi Yu.V., Nezbeda I. Analytical solution of Wertheim's OZ equation for the Smith-Nezbeda model of associated liquids. // Mol. Phys., 1991, vol. 73, No 3, p. 703-713.
[18] Kalyuzhnyi Yu.V., Vlachy V., Holovko M.F., Stell G. Multidensity integral equation theory for highly asymmetric electrolyte solutions. // J. Chem. Phys., 1995, vol. 102, No 14, p. 5770-5780.
[19] Holovko M.F., Kalyuzhnyi Yu.V. On the effects of association in the statistical theory of ionic systems. Analytic solution of the PY-MSA version of the Wertheim theory. // Mol. Phys., 1991, vol. 73, No 5, p. 1145-1157.
[20] Kalyuzhnyi Yu.V., Holovko M.F., Protsykevytch I.A. Solution of the associative Percus-Yevick approximation for n-component mixture of dimerizing hard spheres. // Chem. Phys. Lett., 1993, vol. 215, No 1,2,3, p. 1-4.
[21] Kalyuzhnyi Yu.V., Stell G. Solution of the polymer MSA for the polymerizing primitive model of electrolytes. // Chem. Phys. Lett., vol. 240, p. 157-164.
[22] Gray C.G., Gubbins K.E. Theory of molecular fluids. N.Y., Oxford University Press, 1984, vol. 1, 626 p.

РОЗВ'ЯЗОК ПОЛІМЕРНОГО НАБЛИЖЕННЯ ПЕРКУСА-ЙЕВІКА ДЛЯ ПОЛІМЕРИЗАЦІЇ В ЗІРКОВІ МОЛЕКУЛИ З ДОВІЛЬНОЮ КІЛЬКІСТЮ ГІЛОК

Ю.В.Калюжний

Отримано аналітичний розв'язок полімерного наближення Перкуса-Йевіка для багатокомпонентної суміші асоціативних твердих сфер, які під дією асоціативних сил утворюють полімерні зіркові молекули. Для опису рівноважних властивостей двокомпонентної асоціативної суміші твердих сфер та лінійних ланцюгових молекул запропонована спрощена версія розв'язку, яка представлена комбінацією полімерного наближення Перкуса-Йевіка та так званого наближення ідеального ланцюга. Проведено дослідження структурних властивостей моделі при всіх ступенях асоціації, включаючи граничний випадок повної асоціації, в якому система представлена рідиною зіркових молекул з довільною кількістю гілок.