Density functional approach for inhomogeneous star polymer fluids

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We propose microscopic density functional theory for inhomogeneous star polymer fluids. Our approach is based on fundamental measure theory for hard spheres, and on Wertheim's first- and second-order perturbation theory for the interparticle connectivity. For simplicity we consider a model in which all the arms are of the same length, but our approach can be easily extended to the case of stars with arms of arbitrary lengths.

It has been demonstrated that density functional theory (DFT) is a versatile and powerful tool by which to represent the structural and thermodynamic properties of polymeric fluids [1–6]. Taking into account the level of the physical model, DFT's of polymers can be divided into two main categories. The first category [1,2] involves the so-called coarse-graining procedure [7], in which the degrees of freedom of monomers building the polymer coils are integrated out. The resulting effective pairwise potential between the centers of masses of two molecules is then used in further investigations [8]. An advantage of these models emerges from the possibility of application of theories of simple fluids to describe the polymers.

It is obvious that coarse-grained models lose some information, e.g., a possibility of evaluation of correlation functions between the monomers. From this point of view, models of the second category [5,6,9–12], which explicitly treat the microscopic structure of polymers, seem to be superior. Several microscopic DFT approaches for inhomogeneous chain polymers have been proposed in the literature. Woodward and Yethiraj [3–5] developed a theory that combines weighted density approximation, known from theories of simple fluids, with single-chain Monte Carlo simulations. An alternative DFT of inhomogeneous polymer solutions was formulated by Forsman, Woodward, and Freasier [11]. Their theory is based on the free energy functional resulting from the generalized Flory equation of state and was extended to the case of inhomogeneous solutions of star polymers [12]. However, from the numerical point of view, a very convenient approach was developed by Yu and Wu [6]. This approach is based on Rosenfelds' fundamental measure theory (FMT) [13] and on Wertheim's first-order thermodynamic perturbation theory (TPT1). The theory of Yu and Wu allows for performing quite complex studies because it does not require single-chain Monte Carlo simulations and yields a fully analytical equation of state. This approach [6] has been successfully applied to investigate adsorption, surface phase transitions and capillary condensation in systems involving chain particles [14–16]. It was also extended to the case of inhomogeneous semiflexible and cyclic polyatomic fluids

[9], as well as to binary hard-rod-polymer mixtures [17].

A few years ago Blas and Vega [18] proposed an extension of the associating fluid theory for bulk systems involving branched chain molecules. According to their model, branched molecules are built of chain segments (arms) of tangentially bonded hard spheres connected via articulation vertices, each of them formed by f arms. The excess Helmholtz free energy due to the chain connectivity is separated into two contributions, one accounting for the formation of the articulation vertex, and a second one due to the formation of the arms. The first term has been described by the second-order thermodynamic perturbation theory (TPT2), whereas the formation of chain arms are via TPT1. The principal aim of this work is to generalize the bulk theory of Blas and Vega to the case of inhomogeneous systems. We consider the simplest case of molecules with one articulation vertex. The generalization is carried out by utilizing the formalism of Yu and Wu [6], derived for chain polymers.

We consider an inhomogeneous fluid composed of star molecules, i.e., each molecule is built of a spherical "head" (articulation vertex), and f arms tangentially attached to it. Each arm is just a chain of M_f tangentially jointed segments. Although the numbers M_f can be different, in this paper we study the case in which all the arms are of the same length, $M \equiv M_f$, so that the total number of segments within a molecule is $N = fM + 1$. All the segments are hard spheres of diameter σ. The bonding potential $V_b(\mathbf{R})$ is defined so that $g(\mathbf{R}) = \exp[-\beta V_b(\mathbf{R})]$ is

$$g(\mathbf{R}) = \prod_{i=1}^{f} \frac{\delta(|\mathbf{r}_0 - \mathbf{r}_1^{(i)}| - \sigma)}{4\pi\sigma^2} \prod_{j=1}^{M-1} \frac{\delta(|\mathbf{r}_{j+1}^{(i)} - \mathbf{r}_j^{(i)}| - \sigma)}{4\pi\sigma^2}, \quad (1)$$

where $\mathbf{R} = (\mathbf{r}_0, \{\mathbf{r}_j^{(i)}\})$ with $i = 1, 2, \ldots, f$ and $j = 1, 2, \ldots, M$ denotes the set of segment positions. The articulation vertex is labelled by the subscript 0. All remaining segments are labelled by the superscript (specifying arm) and the subscript (specifying the position within a given arm). The grand potential of the system Ω is as a functional of the local density of polymers, $\rho(\mathbf{R})$,

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$$\Omega[\rho(\mathbf{R})] = F_{\text{id}}[\rho(\mathbf{R})] + F_{ex}[\rho(\mathbf{R})] + \int d\mathbf{R}\rho(\mathbf{R})[V_{\text{ext}}(\mathbf{R}) - \mu], \tag{2}$$

where μ is the configurational chemical potential, V_{ext} is the external potential, $\beta F_{\text{id}}[\rho(\mathbf{R})] = \beta \int d\mathbf{R}\rho(\mathbf{R})V_b(\mathbf{R}) + \int d\mathbf{R}\rho(\mathbf{R})[\ln(\rho(\mathbf{R})) - 1]$ is the ideal part of the free energy and F_{ex} is the excess free energy. The external potential is a sum of the potentials acting on each segment, $V_{\text{ext}}(\mathbf{R}) = v_0(\mathbf{r}_0) + \Sigma_{i=1}^f \Sigma_{j=1}^M v_j^{(i)}(\mathbf{r}_j^{(i)})$. We further assume that the excess free energy is a functional of the average segment local density defined as

$$\rho_s(\mathbf{r}) = \rho_0(\mathbf{r}) + \sum_{i=1}^f \sum_{j=1}^M \rho_j^{(i)}(\mathbf{r}) = \int d\mathbf{R}\,\delta(\mathbf{r} - \mathbf{r}_0)\rho(\mathbf{R})$$

$$+ \sum_{i=1}^f \sum_{j=1}^M \int d\mathbf{R}\,\delta(\mathbf{r} - \mathbf{r}_j^{(i)})\rho(\mathbf{R}), \tag{3}$$

where $\rho_j^{(i)}(\mathbf{r})$ and $\rho_0(\mathbf{r})$ are local densities of segment "j within the arm i" and of the articulation segment, respectively.

Following Yu and Wu [6] we decompose the excess free energy as

$$\beta F_{ex}[\rho_s(\mathbf{r})] = \int d\mathbf{r}[\Phi_{\text{HS}}(\{n_\alpha(\mathbf{r})\}) + \Phi_C(\{n_\alpha(\mathbf{r})\})], \tag{4}$$

where Φ_{HS} results from the hard-sphere repulsion between segments, and Φ_C is the contribution due to the connectivity. Each of these contributions is a function of four scalar and two vector weighted densities [6,13]. For the hard-sphere contribution Φ_{HS} we use the White-Bear theory, see Refs. [19,20] for the explicit formula.

Wertheim's perturbation theory for a bulk fluid [22] can be naturally incorporated into the DFT framework [21]. The generalization for inhomogeneous star polymer systems is represented by the expression [18,23]

$$\Phi_C(\{n_\alpha(\mathbf{r})\}) = \Phi^{\text{arm}}(\{n_\alpha(\mathbf{r})\}) + \Phi^{\text{art}}(\{n_\alpha(\mathbf{r})\}), \tag{5}$$

where Φ^{arm} and Φ^{art} are the contributions due to the formation of chains within consecutive arms and due to the formation of the articulation vertex. The equation for Φ^{arm} follows from the theory of Yu and Wu [6],

$$\Phi^{\text{arm}}(\{n_\alpha(\mathbf{r})\}) = \frac{1 + f - N}{N} n_0 \zeta \ln[y_{\text{HS}}(\sigma, \{n_\alpha(\mathbf{r})\})], \tag{6}$$

where $\zeta = 1 - \mathbf{n}_{V2} \cdot \mathbf{n}_{V2}/(n_2)^2$, and the contact value of the hard-sphere cavity function, $y_{\text{HS}}(\sigma)$, results from the Carnahan-Starling equation of state, cf. Eq. (18) of Ref. [6]. Free energy density Φ^{art} is obtained by generalizing the theory of Blas and Vega [18,23],

$$\Phi^{\text{art}}(\{n_\alpha(\mathbf{r})\}) = \Phi_{\text{TPT1}}^{\text{art}}(\{n_\alpha(\mathbf{r})\}) + \Phi_{\text{TPT2}}^{\text{art}}(\{n_\alpha(\mathbf{r})\}), \tag{7}$$

where $\Phi_{\text{TPT1}}^{\text{art}}$ and $\Phi_{\text{TPT2}}^{\text{art}}$ represent the first

$$\Phi_{\text{TPT1}}^{\text{art}}(\{n_\alpha(\mathbf{r})\}) = -\frac{f}{N} n_0 \zeta \ln[y_{\text{HS}}(\sigma, \{n_\alpha(\mathbf{r})\})], \tag{8}$$

and the second-order perturbation terms [18,22]

$$\Phi_{\text{TPT2}}^{\text{art}} = \ln\sqrt{1 + 4\Lambda} - \ln\frac{(1 + \sqrt{1 + 4\Lambda})^{f+1} - (1 - \sqrt{1 + 4\Lambda})^{f+1}}{2^{f+1}}. \tag{9}$$

In the above Λ depends on the number of arms and its evaluation requires the knowledge of the f-body correlation function for f spheres in contact. In the case of $f=3$ the application of the superposition approximation yields $\Lambda = (1 + an_3 + bn_3^2)/(1 - n_3)^3 - 1$, where a and b are constant that depend on the angles between the arms attached to the articulation vertex [18,22,23]. In the case of bulk fluids n_3 is just the packing fraction. Approximation proposed for inhomogeneous system relies on substitution of the bulk packing fraction by the weighted density n_3. Note that this approximation is not unique. One can follow the ideas of Yu and Wu [20] and propose an approximation involving, besides scalar, also vector weighted densities. In this work, however, we decided to apply as simple expression, as possible.

Within the TPT1 approach the bulk thermodynamic properties of the star polymers are the same as the properties of chains built of the same number of segments. This is because the first-order perturbation free energy takes into account only the number of segment connections and neglects polymer's topology. The latter is included within the TPT2 approach, cf. Eq. (15) of Ref. [18]. However, the identity of the bulk thermodynamic properties within the TPT1 theory does not imply that the structure of inhomogeneous fluids of star polymers and of chains with the same number of segments, that results from DFT, is identical.

Minimization of (2) yields

$$\rho(\mathbf{R}) = g(\mathbf{R})\exp\left(\beta\mu - \beta\lambda_0(\mathbf{r}_0) - \beta\sum_{i=1}^f\sum_{j=1}^M \lambda_j^{(i)}(\mathbf{r}_j^{(i)})\right), \tag{10}$$

where $\lambda_j^{(i)}(\mathbf{r}_j^{(i)}) = \delta F_{ex}/\delta\rho_s(\mathbf{r}_j^{(i)}) + v_j^{(i)}(\mathbf{r}_j^{(i)})$ and $\lambda_0(\mathbf{r}_0) = \delta F_{ex}/\delta\rho_s(\mathbf{r}_0) + v_0(\mathbf{r}_0)$. For systems with the density distribution varying only in the z direction Eqs. (3) and (10) lead to the following expressions for the segment density profiles:

$$\rho_0(z_0) = \exp(\beta\mu)\gamma_0(z_0)(G^{M+1}(z_0))^f \tag{11}$$

and

$$\rho_j^{(i)}(z_j^{(i)}) = \exp(\beta\mu)\gamma_j^{(i)}(z_j^{(i)})G^{M+1-j}(z_j^{(i)})\tilde{G}^{j+1}(z_j^{(i)}), \tag{12}$$

where $\gamma_j^{(i)}(z) = \exp[-\beta\lambda_j^{(i)}(z)]$; $\gamma_0(z) \equiv \gamma_0^{(i)}(z)$. The functions $G^i(z)$ are defined by the recurrence relation [6]

$$G^j(z) = \int dz'\,\gamma_j^{(i)}(z')\frac{\theta(\sigma - |z - z'|)}{2\sigma}G^{j-1}(z'), \tag{13}$$

for $j = 2, \dots, M$ with $G^i(z) \equiv 1$. In the above θ is the unit-step function. The functions $\tilde{G}^j(z)$, however, are given by
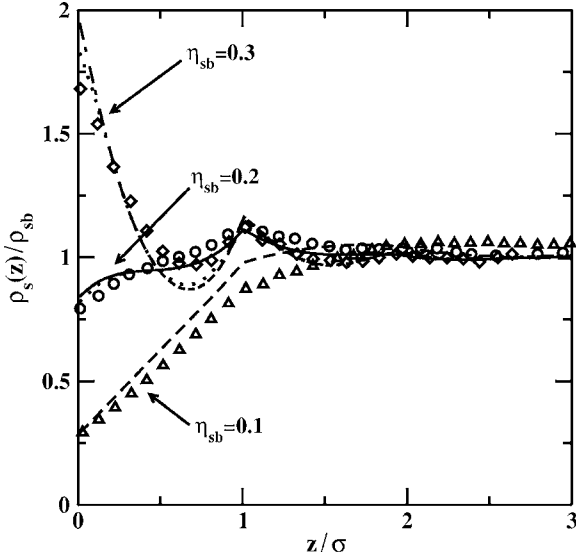
FIG. 1. The average segment density profiles of star polymers ($f=3$, $M=5$) evaluated for the bulk segment packing fraction η_{sb} =0.1, 0.2, and 0.3. Symbols represent computer simulations [24], dashed lines denote DFT results obtained using TPT1 and dots denote DFT results evaluated using TPT1 and TPT2 contributions.

$$\widetilde{G}^2(z) = \int dz' \, \gamma_0(z') \frac{\theta(\sigma - |z - z'|)}{2\sigma} (G^{M+1}(z'))^{f-1}, \quad (14)$$

for $j=2$ and

$$\widetilde{G}^j(z) = \int dz' \, \gamma_j^{(i)}(z') \frac{\theta(\sigma - |z - z'|)}{2\sigma} \widetilde{G}^{j-1}(z'), \quad (15)$$

for $j>2$. The equations given above are valid for the stars with arms of identical length. In such a case the profiles $\rho_j^{(i)}(z)$ are independent of the arm index i. A generalization of the theory to the case of stars with arms of different length is straightforward. For example, the integrand in the last equation would involve a product of the functions $G^{M_1+1}(z')G^{M_2+1}(z')\cdots$, instead of $(G^{M+1}(z'))^{f-1}$ (here M_i's abbreviate the number of segments within consecutive arms). As a simple application of the theory we calculate density profiles of star molecules built of hard-sphere segments near a hard wall, located at $z=0$. The solutions of the density profile equations were obtained by using the standard iterational procedure.

In Fig. 1 we compare the average segment density profiles resulting from theory with computer simulations [24] for star polymers built of $f=3$ arms, each composed of $M=5$ segments. The calculations were carried out for bulk segment packing fractions $\eta_{sb} = \pi\rho_{sb}\sigma^3/6 = 0.1$, 0.2, and 0.3, where ρ_{sb} is the bulk average segment density. The density profiles in Fig. 1 have been normalized by the bulk density ρ_{sb}. For $\eta_{sb}=0.2$ and 0.3 we show two sets of the DFT results. The first one has been evaluated employing the TPT1 approach [i.e., the term given in Eq. (9) has been neglected], whereas the second set was obtained using TPT1 and TPT2 contributions to the free energy. The differences between the local densities resulting from these two approximations are small
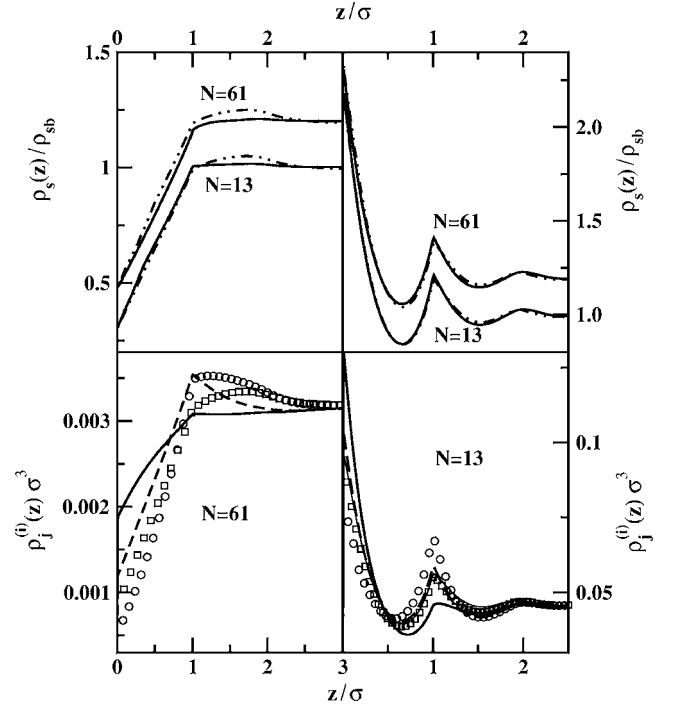

FIG. 2. Upper panels, the average segment density profiles of star polymers (dashed-dotted lines) and of chains (solid lines) calculated for the total number of segments $N=13$ and $N=61$. The results for $N=61$ are shifted up by 0.2. Lower panels, the segment density profiles of the articulation segment (circles) and of its nearest neighbor (squares) of star polymers and of the first (solid lines) and the second (dashed lines) segment of chains. In the left panels, $\rho_{sb}^*=0.2$, whereas $\rho_{sb}^*=0.6$ in the right panels.

and occur only within the region adjacent to the wall. The TPT2 contribution leads to smaller contact values of the average segment local density. This effect is quite obvious, because the TPT2 correction lowers the pressure. The agreement between theoretical predictions and computer simulations is reasonable.

Figure 2 compares the density profiles for three-armed star polymers (resulting from the TPT1 approach) with the profiles of chain polymers built of the same number of segments obtained from the approach of Yu and Wu [6]. The results are for bulk average segment densities $\rho_{sb}^*=\rho_{sb}\sigma^3$ =0.2 and 0.6 and for two model systems with different total number of segments $N=13$ and $N=61$. For $N=13$ each star polymer arm is composed of $M=4$ segments, whereas for $N=61$ each arm consists of $M=20$ segments. In the upper panels we compare the average segment densities normalized to unity. We find that for higher bulk density $\rho_{sb}^*=0.6$ (the upper right-hand-side panel) the local densities $\rho_s(z)$ of chains and stars are quite similar. The profiles are dominated by packing effects. Larger differences between the profiles of the star and chain polymer fluids are visible at lower density, $\rho_{sb}^*=0.2$, cf. the upper left-hand-side panel. Note that the contact values of $\rho_s(z)$ for star and chain polymers are identical in our TPT1 approach. Lower panels of Fig. 2 show the density profiles of selected segments for the same systems. We plot here the profiles of "heads" (in the case of chains the profiles of the first segment) and the profiles of the segments

attached directly to the "heads." The differences between the profiles for the chain and star polymers are now more pronounced, especially for the profiles of the "heads." We have also inspected the profiles for the segments that are topologically more distant from the head and have found that the difference between them becomes gradually smaller.

Finally, Fig. 3 presents the profiles of the stars built of the same number of segments, but having different number of arms. We have considered the models with $f=3, M=20$ and with $f=4, M=15$. It is not surprising that the difference between the average segment density profiles [cf. Fig. 3(a)] is now less pronounced than in the case of the profiles displayed in Fig. 2, because the differences in the topology of the particles are now smaller. However, the differences between the individual segment density profiles still persist, cf. Fig. 3(b), where we show the profiles of "heads" and the segments directly attached to heads.

In conclusion, in this work we propose density functional theory for inhomogeneous star polymers. Although the theory is written down for the case of arms composed of identical numbers of segments, its generalization for stars with arms of different length is straightforward. Several further extensions are also possible. In particular it would be of interest to consider cases of physically different "head" and "arm" segments in order to mimic the systems involving surfactants. Some of these topics are already under study in our laboratory.
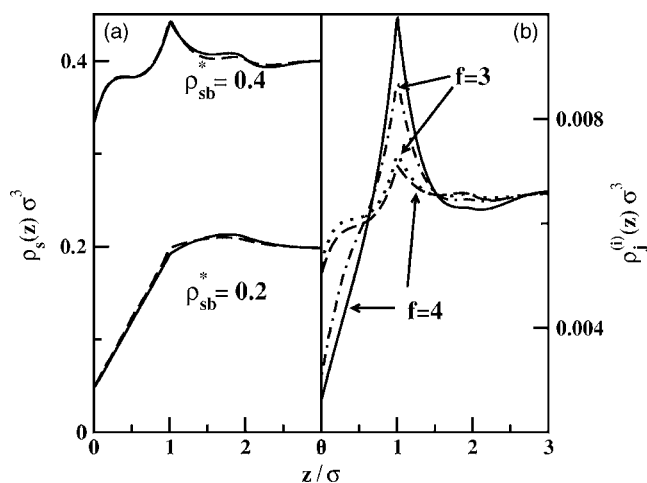

FIG. 3. (a) The average segment density of star polymers with $f=3$ and $M=20$ (dashed line) and with $f=4$ and $M=15$ (solid line) for two bulk densities, $\rho_{sb}^*=0.2$ and $\rho_{sb}^*=0.4$. (b) The segment density profiles of "heads" (solid and dashed-dotted lines) and it's first neighbor (dashed and dotted lines) for the same models. The bulk segment density is $\rho_{sb}=0.4$.

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