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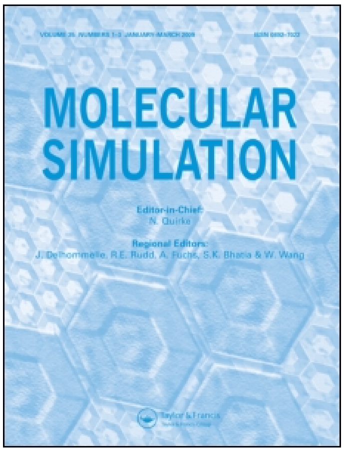

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Density Functional Theory of Square-well Chain Mixtures Near Solid Surface

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A density functional theory is developed for square-well chain mixtures near a hard wall or a square-well wall. The Helmholtz free energy functional is divided into two parts, an ideal-gas contribution and an excess contribution. The later is constructed based on weighting density approximation and coarse graining approximation. For simplicity, a Heaviside function is used as the weighting function. To calculate the density profiles of beads, a direct iterative algorithm combined with a relaxation factor is used. A single chain simulation in an effective field is needed in each iterative step. The theoretical results are in good agreement with Monte Carlo simulation.

Keywords: Density functional theory; Square-well chain mixture; Reference interaction site model; Helmholtz energy

INTRODUCTION

The first density functional theory (DFT) for polymers were developed by Chandler, McCoy and Singer (CMS) [1,2], which is a direct extension of the standard DFT of simple fluid based on the theory of reference interaction site model (RISM) [3]. Nath *et al.* [4] used the polymer RISM to construct a density expansion of the free energy functional. Woodward [5] developed another class of density functional theories where the free energy functional of a real polymer system was divided into an ideal part and an excess part. Yethiraj and Woodward [6,7] then established a DFT in which the coarse graining approximation and the weighting function are used to construct the excess part of the free energy functional. More recently, Hooper *et al.* [8,9] introduced into the DFT theory an efficient algorithm that permitted the single chain simulation to be taken out of the iterative loop. Kierlik and Rosinberg [10–12] extended the thermodynamic perturbation theory to nonuniform polymer system. Their theory is similar to the generalized van der Waal's DFT [5]. Cai *et al.* [13] combined Kierlik *et al.*'s DFT [12] with coarse grain approximation and got the same expressions as that of Yethiraj and Woodward [6]. For a polymer system with attractive interactions, Patra and Yethiraj [14] present a DFT associated generalized van der Waals DFT with WDA. McMullen and Freed [15] have derived a density-functional formulation from basic statistical mechanics relations. Zhou [16] developed a DFT for a nonuniform single-component freely jointed tangential hard-sphere polymer.

The density functional theories have also been generalized to mixtures. For simple fluid mixtures, there are several kinds of DFTs such as Choudhury and Ghosh's [17], Denton and Ashcroft's [18] and Patra's [19] formalism. Cai *et al.* [20] developed a theory for the polymer mixture and extended it into tangentially jointed hard-sphere chain mixtures. In this work, we will present a DFT for the mixtures of square-well chain mixtures based on WDA.

DFT OF THE MIXTURES OF CHAIN-LIKE MOLECULES

For simple fluids, DFT is based on the fact that the grand potential, Ω, can be expressed as a functional of the local density $\rho(\mathbf{r})$. The real density distribution minimizes the grand potential. For a one-component chain system, the grand potential can be

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expressed as:

$$\Omega[\rho_M(\mathbf{R})] = F[\rho_M(\mathbf{R})] + \int (V_M(\mathbf{R}) - \mu_M)\rho_M(\mathbf{R})\,\mathrm{d}\mathbf{R} \qquad (1)$$

where $\mathbf{R}$ denotes the positions of all m monomers on a polymer molecule, $\rho_M(\mathbf{R})$ is the molecule density as a function of these positions, μ_M is the chemical potential, $F[\rho_M(\mathbf{R})]$ is the free energy functional and $V_M(\mathbf{R})$ is the external field. At equilibrium, Ω satisfies:

$$\frac{\delta\Omega[\rho_M(\mathbf{R})]}{\delta\rho_M(\mathbf{R})} = 0. \qquad (2)$$

According to Woodward [5], the Helmholtz free energy functional $F[\rho_M(\mathbf{R})]$ can be separated into two parts, an ideal term and an excess term

$$F[\rho_M(\mathbf{R})] = F^{id}[\rho_M(\mathbf{R})] + F^{\mathrm{ex}}[\rho_M(\mathbf{R})]. \qquad (3)$$

In this work, we consider a mixture of L homopolymers. The monomers of different kinds of molecules can be different. In this case, the symbol ρ_M should be regarded as $\rho_M = (\rho_{M,1}, \rho_{M,2}, \ldots, \rho_{M,L})$. The ideal part of the Helmholtz energy functional is given by

$$F^{\mathrm{id}}[\rho_M] = kT\sum_{l=1}^{L}\int \rho_{M,l}(\mathbf{R}_l)\Big[\ln\rho_{M,l}(\mathbf{R}_l) - 1 + V_{M,l}(\mathbf{R}_l) + U_{M,l}(\mathbf{R}_l)\Big]\,\mathrm{d}\mathbf{R}_l. \qquad (4)$$

The chemical potential of the molecule $\mu_{M,l}$ can be expressed as the functional derivative of the Helmholtz free energy functional

$$\mu_{M,l} = kT\ln\rho_{M,l}(\mathbf{R}_l) + U_{M,l}(\mathbf{R}_l) + V_{M,l}(\mathbf{R}_l) + \frac{\delta F^{\mathrm{ex}}[\rho_M]}{\delta\rho_{M,l}(\mathbf{R}_l)}. \qquad (5)$$

Thus, we obtain the density profiles of the molecules

$$\rho_{M,l}(\mathbf{R}_l) = \exp\left[\beta\mu_{M,l} - \beta U_{M,l}(\mathbf{R}_l) - \beta V_{M,l}(\mathbf{R}_l) - \frac{\delta\beta F^{\mathrm{ex}}[\rho_M]}{\delta\rho_{M,l}(\mathbf{R}_l)}\right] \qquad (6)$$

where $\beta = 1/kT$. The calculation and description of the density profile of molecules is complicated; therefore, the bead density is defined

$$\rho_l(\mathbf{r}) = \int\sum_{j=1}^{m_l}\rho_{M,l}(\mathbf{R}_l)\delta(\mathbf{r} - \mathbf{r}_j)\,\mathrm{d}R_l \qquad (7)$$

where ρ_l is the density profile of the bead of molecule l and m_l is the chain length of the component l. Because the monomers of different molecules are different, each kind of molecule consists of only one kind of monomer, so the subscript indexes of molecules and monomers are the same. Thus, the functional derivative in Eq. (6) is given by

$$\frac{\delta\beta F^{\mathrm{ex}}[\rho_M]}{\delta\rho_{M,l}(\mathbf{R}_l)} = \int\frac{\delta\beta F^{\mathrm{ex}}[\rho_M]}{\delta\rho_l(\mathbf{r}')}\frac{\delta\rho_l(\mathbf{r}')}{\delta\rho_{M,l}(\mathbf{R}_l)}\,\mathrm{d}r'. \qquad (8)$$

Substitute Eq. (7) into Eq. (8), we have

$$\frac{\delta\beta F^{\mathrm{ex}}[\rho_M]}{\delta\rho_{M,l}(\mathbf{R}_l)} = \sum_{j=1}^{m_l}\int\frac{\delta\beta F^{\mathrm{ex}}[\rho_M]}{\delta\rho_l(\mathbf{r}')}\delta(\mathbf{r} - \mathbf{r}_j)\,\mathrm{d}r'. \qquad (9)$$

However, the Helmholtz energy functional is not known and the approximation should be introduced. The coarse graining approximation is used to construct the Helmholtz energy functional in this work

$$F^{\mathrm{ex}}[\rho_M] = \sum_{i=1}^{K}\int\rho_i(\mathbf{r})f_i(\bar{\rho}(\mathbf{r}))\,\mathrm{d}r \qquad (10)$$

where $\bar{\rho}(\mathbf{r}) = (\bar{\rho}_1(\mathbf{r}), \bar{\rho}_2(\mathbf{r}), \ldots, \bar{\rho}_L(\mathbf{r}))$ are the weighted density. The partial molecular excess Helmholtz energy of homogeneous fluid f_i is given by

$$f_i = \left(\frac{\partial F^{\mathrm{ex}}}{\partial\rho_i}\right)_{T,p,\rho_{j\neq i}} \qquad (11)$$

where T and P are temperature and pressure of the system, respectively. Note that the derivative is calculated with respect to the density of beads, not molecules. To avoid the ambiguity encountered in calculating the partial molecular quantities, we assume that beads on different kinds of molecules are different, albeit they may be the same monomers. Thus, Eq. (9) becomes

$$\frac{\delta\beta F^{\mathrm{ex}}[\rho_M]}{\delta\rho_{M,l}(\mathbf{R}_l)} = \sum_{j=1}^{m_l}\left[\beta f_l(\bar{\rho}(\mathbf{r}_j)) + \int\rho_l(\mathbf{r})\frac{\partial\beta f_l(\bar{\rho}(\mathbf{r}))}{\partial\bar{\rho}_l(\mathbf{r})}\frac{\delta\bar{\rho}_l(\mathbf{r})}{\delta\rho_l(\mathbf{r}_j)}\,\mathrm{d}\mathbf{r}\right]. \qquad (12)$$

Let

$$\lambda_i(\mathbf{r}) = \beta f_i(\bar{\rho}(\mathbf{r})) + \sum_{s=1}^{K}\sum_{t=1}^{K}\int\rho_s(\mathbf{r}')\frac{\partial\beta f_s(\bar{\rho}(\mathbf{r}'))}{\partial\bar{\rho}_t(\mathbf{r}')}\frac{\delta\bar{\rho}_t(\mathbf{r}')}{\delta\rho_i(\mathbf{r})}\,\mathrm{d}\mathbf{r}'. \qquad (13)$$

Substituting Eqs. (6), (12) and (13) into Eq. (7), we obtain the density profile of the beads:

$$\rho_l(\mathbf{r}) = \int\sum_{j=1}^{m_l}\delta(\mathbf{r} - \mathbf{r}_j) \times \exp\left[\beta\mu_{M,l} - \beta U_{M,l}(\mathbf{R}_l) - \beta V_{M,l}(\mathbf{R}_l) - \sum_{k=1}^{m_l}\lambda_l(\mathbf{r}_k)\right]\mathrm{d}R_l. \qquad (14)$$

Yethiraj and Woodward [6] have demonstrated that for hard-sphere chain fluid the weighted density can be calculated using a very simple weighting function without losing much accuracy.

$$\bar{\rho_l}(\mathbf{r}) = \int \rho_l(\mathbf{r}')w_l(|\mathbf{r}-\mathbf{r}'|)\,\mathrm{d}\mathbf{r}' \tag{15}$$

where $w_l(\mathbf{r})$ is the weighting function given by

$$w(r) = \frac{3}{4\pi\sigma_l^3}\Theta(\sigma_l - r) \tag{16}$$

where σ_l is the diameter of monomers, Θ is the Heaviside function. A sophisticated weighting function was proposed by Yethiraj [7] based on PRISM. In this work, Yethiraj *et al.*'s [6] simple weighing function, Eq. (16), is used.

For the mixture of square-well chain fluids, the free energy functional is consisted of a term arising from the contribution of the mixture of hard sphere chains and a perturbation term arising from the square-well interaction between beads. In this work, the molecular thermodynamic model developed by Hu *et al.* [22] is used for the former and Alder *et al.*'s molecular dynamics simulation results are used for the latter.

The numerical algorithm consists of a single-chain simulation and iterative calculations. The former can be used to calculate the density profile given by Eq. (14). The iterative procedure adopted is a kind of Picard method. We start our calculation with an initial guess for the density profile, usually the average density of the beads. Then we calculate $\lambda_i(\mathbf{r})$ using Eq. (13) and a new density profile is obtained using Eq. (14). Next, mix the new values and the old with a relaxation factor and renormalize the results to the average density in the slit. We repeat those steps until the accuracy is approached.

MONTE CARLO SIMULATION

We use the Dickman–Hall [21] algorithm for the canonical Monte Carlo simulations. The procedure for simulation is as follows. First, the initial configuration of the copolymer is generated by an off-lattice self-avoiding random walk. Second the chain is subjected to a translation in the external fields. Third, the chain is subjected to a "translate-jiggle" movement. A bond is chosen randomly on the chain. Then, randomly choose either end (e.g. segment *i*) of the bond to be stationary and make the other end of the bond (segment $i-1$) translate a certain distance. Then, normalize the distance between these two segments to be the bond length, i.e. normalize $r_{i-1,i}$ to σ. The sub-chain (segments 1, $2\ldots i-2$) that is connected to segment $i-1$ is subjected to the same translation as that for segment $i-1$. The Metropolis algorithm is used to decide if the movement is accepted or not. Then, a procedure similar to moving segment $i-1$ is applied repeatedly to segment $i-2$ and so on until the end of the chain.

The average volume fraction η_{avg} in simulation cell is calculated by

$$\eta_{\text{avg}} = \frac{\pi}{6V}\sum_{l=1}^{L} N_l\sigma_l^3 \tag{17}$$

L is the number of species of square-well sphere, N_l is the number of each kind of spheres, V is the volume of the simulation cell and σ_l is the diameter of the corresponding sphere.

The interaction between chain segments is described by a square-well potential

$$\beta u(r_{ij}) = \begin{cases} 0 & r_{ij} > R\sigma_{ij} \\ -\beta\varepsilon & \sigma_{ij} < r_{ij} \le R\sigma_{ij} \\ \infty & r_{ij} \le \sigma_{ij} \end{cases} \tag{18}$$

where ε is the well depth, r_{ij} is the distance between the centers of hard spheres. The walls are impenetrable to the center of the square-well spheres with the bead–wall interaction potential $u_{i-\text{wall}}$

$$\beta u_{i-\text{wall}}(r_{i-\text{wall}}) = \begin{cases} 0; & r_{i-\text{wall}} \ge \sigma \\ -\beta\varepsilon_{i-\text{wall}}; & 0 \le r_{i-\text{wall}} < \sigma \\ +\infty; & r_{i-\text{wall}} < 0 \end{cases} \tag{19}$$

where $r_{i-\text{wall}}$ is the distance from the center of the bead to the wall; $R = 1.5$ is the reduced width of the square-well; $\varepsilon_{i-\text{wall}}$ is the well depth; kT/ε is the reduced temperature denoted by T^*. The total potential energy of the system is the sum of the potential energy between all pairs of beads and that between beads and walls.

RESULTS AND DISCUSSIONS

The following results concern the density distribution of hard-sphere chains and square-well chains. The chains are confined in a slit of width 10σ, σ is the diameter of the hardcore of the bead. The wall is a hard wall or a square-well wall described as Eq. (19). In this work, we use $\beta\varepsilon_{i-\text{wall}} = 0.1$, $T^* = 6.0$.

To calculate the excess free energy, the equation of state for hard-sphere chain fluids suggested by Hu *et al.* [22] and that for square-well chain fluids suggested by Liu and Hu [23] are adopted.

Hard-sphere Chain Fluids

Figure 1 shows the monomer density profiles of the mixtures of 3 and 12-mer hard-sphere chains

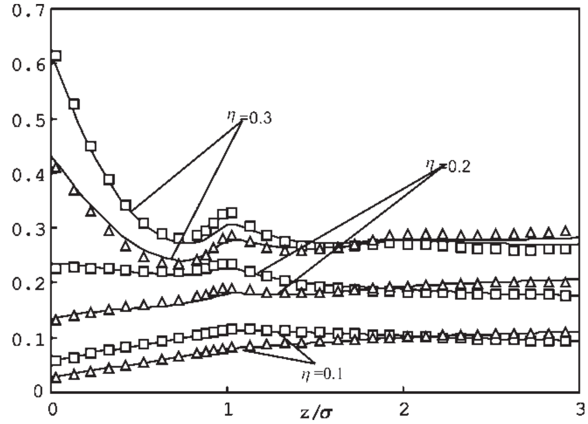

FIGURE 1 Density profiles of 3 and 12-mer hard-sphere chains with the mole fraction of 3-mer 0.5 confined in two hard walls. Lines: theory, square: MC for 3-mer, triangle: MC for 12-mer.

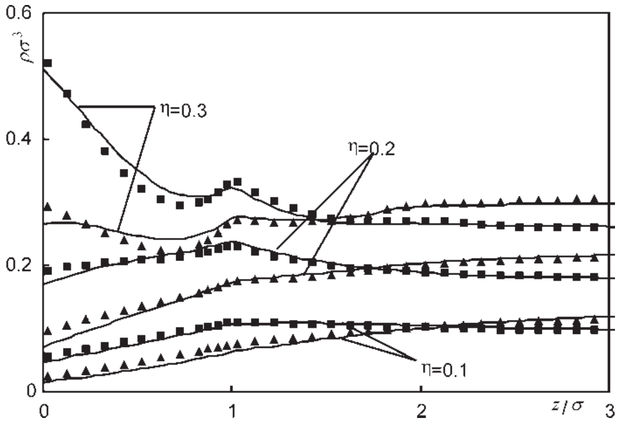

FIGURE 3 Density profiles of 3 and 12-mer square-well chains with the mole fraction of 3-mer 0.5 confined in two hard walls. Lines: theory, square: MC for 3-mer, triangle: MC for 12-mer, $T^* = 6.0$.

between two hard walls. The mole fraction of 3-mer is 0.5 and the average packing density varies from $\eta = 0.1$ to 0.3. The predicted results are in good agreement with those by simulation. At higher bulk densities, the density profiles of hard-sphere chains are similar to that of simple hard spheres, which has a high peak near the wall and a decayed oscillation towards central phase. This oscillation tends to be insignificant beyond 3σ. At lower bulk densities, the density profiles exhibit a small peak at about 1σ instead of a high peak near the wall. As the bulk density further decreases, the peak tends to disappear. The variation of bead density near the wall results from the competition between the configurational entropic effect and the bulk packing effect. For HSCFs, the loss in configurational entropy promotes the depletion of beads near the surface while the packing of chains against surface promotes enrichment. At low densities, the configurational entropic effect plays a key role. At high densities, the bulk packing effect dominates to utilize the available free volume more efficiently.

Figure 2 shows the monomer density profiles of the same mixtures as Fig. 1 between two square-well walls. Just as in Fig. 1, the density profile has a high peak near the wall and a decayed oscillation towards central phase. Beside the configurational entropic effect and the bulk packing effect, the attractive potential of the square-well walls should not be omitted when considering the bead density near the wall.

Square-well Chain Fluids

Figures 3 and 4 show the monomer density profiles of the mixtures of 3 and 12-mer square-well chains between two hard walls and between two square-well walls. The mole fraction of 3-mer is 0.5 and the average packing density varies from $\eta = 0.1$ to 0.3. The comparison between the predicted values and

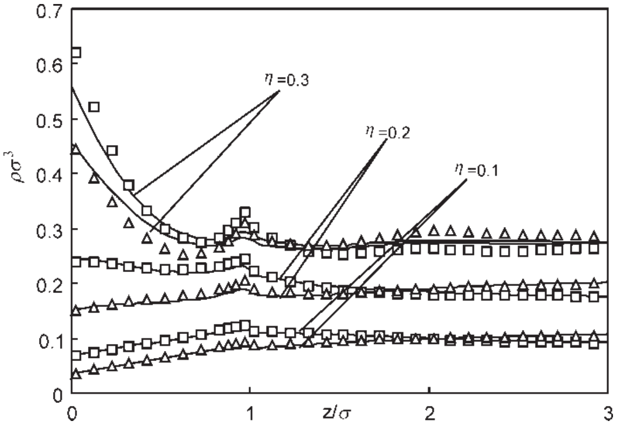

FIGURE 2 Density profiles of 3 and 12-mer hard-sphere chains with the mole fraction of 3-mer 0.5 confined in two square-well walls. Lines: theory, square: MC for 3-mer, triangle: MC for 12-mer, $\beta\varepsilon_{i-\text{wall}} = 0.1$.

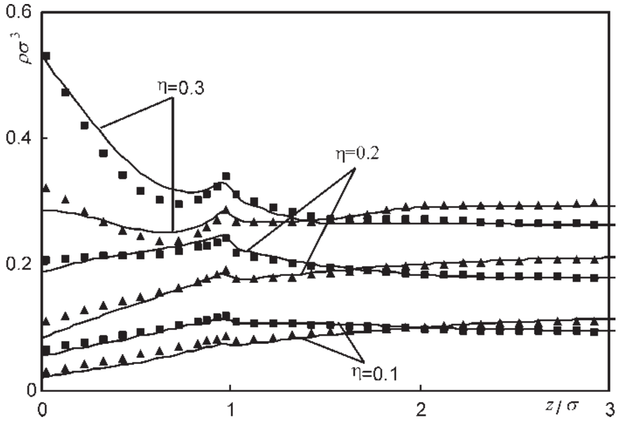

FIGURE 4 Density profiles of 3 and 12-mer square-well chains with the mole fraction of 3-mer 0.5 confined in two square-well walls. Lines: theory, square: MC for 3-mer, triangle: MC for 12-mer, $\beta\varepsilon_{i-\text{wall}} = 0.1$, $T^* = 6.0$.

those of simulation is the same as those in Figs. 1 and 2.

CONCLUSIONS

In this work, we show a density functional theory based on weighting density approximation and coarse graining approximation. We present the results for the mixtures of hard-sphere chains and square-well chains based on our theory. For the walls' potential, hard walls and square-well walls are considered. Although the weighting function is simple, for both hard-sphere chains and square-well chains, the results predicted by our theory are in good agreement with those by simulation. The monomer density profiles of mixtures are similar to those of the pure component in the same condition. The transition from depletion to enhancement occurs at different bulk densities depending on the chain length, longer chains prefer the higher transition density. This is also the case for the mixtures even if there were two different kinds of chains.

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