

Structure of nonuniform polymer melts: Density functional perturbation approach

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A density functional perturbation approximation for polyatomic molecules, which is based on the fundamental-measure theory for hard-core repulsion and the hybrid weighted-density approximation for chain connectivity, was proposed to clarify the structure of polymer melts at interfaces. It was applied to predict the local density distributions, adsorption isotherms, and surface excess of a freely jointed tangent hard-sphere chain in hard slit pores. Wertheim's first-order perturbation theory extended by Yu and Wu [J. Chem. Phys. **112**, 2368 (2002)] was used to calculate the weight function and second-order direct correlation function due to the chain connectivity. The theoretical results are in excellent agreement with the computer simulations.

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The structural behaviors of polymer melts at interfaces are of considerable practical application such as lubrication, surface finishing, and liquid polymer alloys [1,2]. Many theoretical approaches like integral equation theory (IET) and density functional theory (DFT) have been developed to understand the effect of polymer structure on their surface properties [1]. Each theory has advantages and disadvantages for the analysis of polymer fluids and solutions. It is generally known that the DFT yields better results than the IET in many applications. Although the DFT is less accurate than computer simulations, it provides a powerful theoretical tool to analyze the polyatomic molecular liquids. Indeed, they can offer a compromise between accuracy and computational expense.

Yu and Wu [3] have recently proposed a density functional perturbation theory (DFPT) analysis of a freely jointed tangent hard-sphere chain in hard slit pores. Here, the contribution due to the chain connectivity is evaluated by using Wertheim's first-order perturbation theory [4] which was extended to inhomogeneous systems in the form of fundamental-measure theory (FMT) weight densities [5]. In particular, Wertheim's first-order perturbation theory extended by Yu and Wu is very accurate for a wide range of density distributions and provides self-consistent solutions for the structural properties of polymer fluids such as the second-order direct correlation function (DCF) $c^{(2)}(r, \rho)$. On the other hand, the success of the DFT's based on the weighted-density approximations (WDA's) [6–9] suggests the application of the DFPT, which is based on the WDA for the chain connectivity, to the case of polymer melts at solid-liquid interfaces.

In this brief report, we will propose a DFPT based both on the reduced excess free energy density for the hard-core repulsion and on the hybrid weighted-density approximation (HWDA) for the chain connectivity to analyze polyatomic fluids. We apply it to study the structural properties of a

freely jointed tangent hard sphere chain at solid-liquid interfaces. We finally discuss the strengths and weaknesses of the proposed DFPT in the actual applications.

We consider a one-component fluid of chain molecules composed of N identical monomeric units. The molecular density $\rho_p(\vec{R})$ is a function of the positions $\vec{R} \equiv \{\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N\}$, which is the set of positions of the monomers on a polymer molecule. The grand potential $\Omega[\rho_p(\vec{R})]$, which is a functional of the molecular density $\rho_p(\vec{R})$, is defined as the Legendre transform of the intrinsic Helmholtz free energy functional $F[\rho_p(\vec{R})]$,

$$\Omega[\rho_p(\vec{R})] = F[\rho_p(\vec{r})] + \int d\vec{R} \rho_p(\vec{R}) [u_{ext}(\vec{R}) - \mu], \quad (1)$$

where μ is the molecular chemical potential and $u_{ext}(\vec{R})$ the external potential responsible for the density inhomogeneity [1]. Following the DFPT, we can divide the intrinsic Helmholtz free energy into three parts; the ideal gas contribution $F_{id}[\rho_p(\vec{R})]$, the excess free energy $F_{hs}[\rho_p(\vec{R})]$ due to the hard-sphere repulsion, and the excess free energy $F_{chain}[\rho_p(\vec{R})]$ due to the chain connectivity. The ideal gas contribution $F_{id}[\rho_p(\vec{R})]$ is given by the exact expression $F_{id}[\rho_p(\vec{R})] = \beta^{-1} \int d\vec{R} \rho_p(\vec{R}) [\ln\{\Lambda^3 \rho_p(\vec{R})\} - 1] + \int d\vec{R} V(\vec{R}) \rho_p(\vec{R})$, where $\beta = 1/k_B T$, k_B is the Boltzmann constant, Λ is the thermal de Broglie wavelength, and $V(\vec{R})$ describes the internal potential corresponding to an arbitrary configuration of a polymer chain.

The equilibrium molecular density satisfies the stationary condition $\delta\beta\Omega[\rho_p(\vec{R})]/\delta\rho_p(\vec{R}) = 0$, which leads to the Euler-Lagrange relation $\mu - u_{ext}(\vec{R}) = \delta\beta F[\rho_p(\vec{R})]/\delta\rho_p(\vec{R})$. For the polymer system whose segments are identical, the local density distribution (or the single particle average site density) $\rho(\vec{r})$ is related to the polymer molecular density $\rho_p(\vec{R})$ via

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$$\rho(\vec{r}) = \int d\vec{R} \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) \rho_p(\vec{R}). \quad (2)$$

Then, the density profile equation becomes

$$\rho(\vec{r}) = \xi \int d\vec{R} \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) \exp \left[-\beta V(\vec{R}) - \beta u_{ext}(\vec{R}) + \sum_{i=1}^N \{c_{hs}^{(1)}(\vec{r}_i; [\rho]) + c_{chain}^{(1)}(\vec{r}_i; [\rho])\} \right], \quad (3)$$

where ξ is the fugacity. $c_{hs}^{(1)}(\vec{r}_1; [\rho])$ and $c_{chain}^{(1)}(\vec{r}_1; [\rho])$ are the first-order direct correlation functions (DCF's) and are defined as the density functional derivative of the excess free energy with respect to the local density distribution. It is well known that for hard spheres, the fundamental-measure theory (FMT) [5] proposed by Rosenfeld and co-workers is numerically simple and very accurate for a wide range of density distributions.

To approximate the first-order DCF $c_{chain}^{(1)}(\vec{r}; [\rho])$ due to the chain connectivity, we introduce the HWDA which was proposed by Leidl and Wagner [10] and applied for studying the structural properties of a confined hard-sphere fluid. Actually, for the hard-sphere fluids within slit pores the HWDA yields good agreement with the computer simulations even for the high densities. Following the HWDA, the excess free energy $F_{chain}[\rho]$ can be written by

$$F_{chain}[\rho] = \int d\vec{r} \rho(\vec{r}) f_{chain}[\bar{\rho}(\vec{r})], \quad (4)$$

where $f_{chain}(\rho)$ is the excess free energy per particle and the weighted density $\bar{\rho}(\vec{r})$ is assumed as

$$\bar{\rho}(\vec{r}_1) = \int d\vec{r}_2 \rho(\vec{r}_2) \omega(\vec{r}_1 - \vec{r}_2; \hat{\rho}) \quad (5)$$

with $\hat{\rho}[\rho] = 1/N \int d\vec{r}_1 \rho(\vec{r}_1) \int d\vec{r}_2 \rho(\vec{r}_2) \omega(\vec{r}_1 - \vec{r}_2; \hat{\rho})$. The weight function $\omega(\rho)$ due to the chain connectivity was specified by the definition of the second-order DCF $c_{chain}^{(2)}(\vec{r}_1 - \vec{r}_2, \rho) \equiv -\delta^2 \beta F_{chain}[\rho] / \delta \rho(\vec{r}_1) \delta \rho(\vec{r}_2) |_{\rho(\vec{r}) \rightarrow \rho}$. In Fourier space, the weight function satisfies the simple algebraic form

$$\rho f_{chain}''(\rho) \omega(k, \rho) \omega(k, \rho) + 2f_{chain}'(\rho) \omega(k, \rho) + \beta^{-1} c_{chain}^{(2)}(k, \rho) = 0. \quad (6)$$

The normalization $\omega(k=0, \rho) = 1$ ensures the compressibility rule [10]. Then, the first-order DCF $c_{chain}^{(1)}(\vec{r}; [\rho])$ becomes, from Eqs.(4) and (5),

$$c_{chain}^{(1)}(\vec{r}_1; [\rho]) = f_{chain}[\bar{\rho}(\vec{r}_1)] + \int d\vec{r}_2 \rho(\vec{r}_2) f_{chain}'[\bar{\rho}(\vec{r}_2)] \frac{\delta \bar{\rho}(\vec{r}_2)}{\delta \rho(\vec{r}_1)}, \quad (7)$$

where the prime denotes the derivative with respect to the density. In the uniform limit, it becomes $c_{chain}^{(1)}(\rho) = f_{chain}(\rho) + \rho f_{chain}'(\rho)$ since $\bar{\rho}[\rho] = \rho$ and $\int d\vec{r} \omega(r, \rho) = 1$.

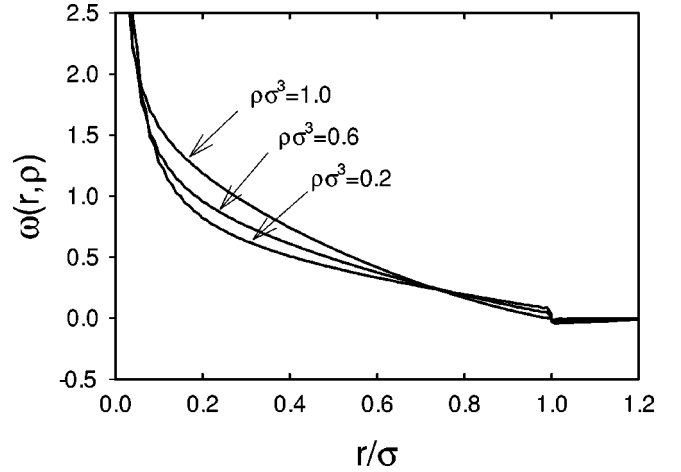


FIG. 1. Weight functions $\omega(r, \rho)$ as a function of the bulk density ρ .

As an application, we consider freely jointed tangent hard-sphere chains at polymer-solid interfaces. In a tangentially connected chain, the bond length is equal to the hard-sphere segment diameter σ and there is no angle constraint between neighboring bonds. The chain connectivity is represented by the bonding potential. Two types of wall-polymer interactions have been considered. One is a structureless hard wall. The other is the hard walls with a slit pore width H . In this case, the external potential is given by $u_{ext}(z) = 0$ for $0 < z < H$. For the polymer systems within slit pores, the local density distribution varies only along the z direction by the symmetry; $\rho(\vec{r}) = \rho(z)$. The local density distribution, Eq. (3), simply becomes, after some manipulations,

$$\rho(z) = \xi \sum_{i=1}^N \exp\{c_{hs}^{(1)}(z; [\rho]) + c_{chain}^{(1)}(z; [\rho])\} G^i(z) G^{N+1-i}(z), \quad (8)$$

where $G^i(z_1) = \int dz_2 \exp\{c_{hs}^{(1)}(z_2; [\rho]) + c_{chain}^{(1)}(z_2; [\rho])\} \theta(\sigma - |z_1 - z_2|) / 2\sigma G^{i-1}(z_2)$ with $G^1(z) = 1$.

The FMT proposed by Rosenfeld and co-workers [5] was employed to calculate the first-order DCF $c_{hs}^{(1)}(\vec{r}; [\rho])$ due to the hard-sphere repulsion. The excess free energy $f_{chain}(\rho)$ and second-order DCF $c_{chain}^{(2)}(r, \rho)$ due to the chain connectivity were evaluated by using the Wertheim's first-order perturbation theory [4] which was extended (using FMT-style weight densities) by Yu and Wu [3,11] to inhomogeneous systems,

$$F_{chain}[\rho] = \frac{1-N}{N} \int d\vec{r} n_0(\vec{r}) \xi(\vec{r}) \ln[y_{hs}(\sigma, \{n_\alpha(\vec{r})\})], \quad (9)$$

where $n_\alpha(\vec{r})$ are the weighted densities, $\xi(\vec{r}) = 1 - \tilde{n}_{V2}(\vec{r}) \cdot \tilde{n}_{V2}(\vec{r}) / n_2^2(\vec{r})$, while $y_{hs}(\sigma, \{n_\alpha(\vec{r})\})$ is connected with the Carnahan-Starling expression for the contact value of the radial distribution function of a hard sphere; $y_{hs}(\sigma, \{n_\alpha(\vec{r})\}) = 1 / [1 - n_3(\vec{r})] + n_2(\vec{r}) \sigma \xi(\vec{r}) / \{4[1 - n_3(\vec{r})]^2 + n_2^2(\vec{r}) \sigma^2 \xi(\vec{r}) / \{72[1 - n_3(\vec{r})]^3\}}$. It is noted that the second-order DCF $c_{chain}^{(2)}(r, \rho)$ depends only on the the scalar weighted den-

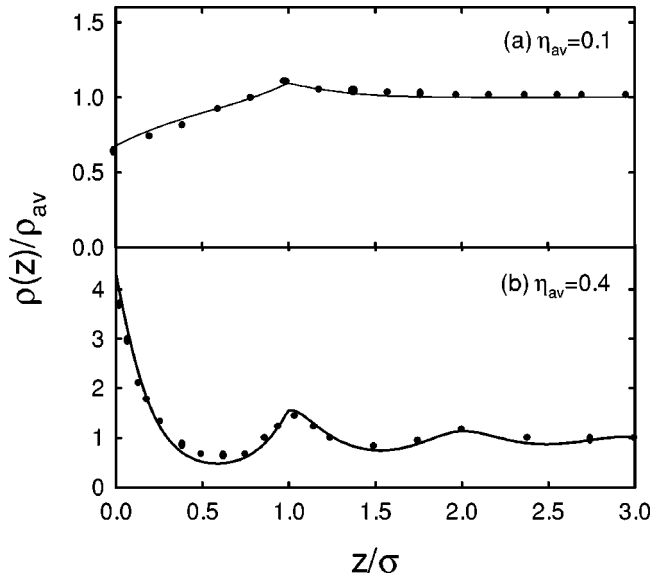


FIG. 2. Local density distributions of tri-mers in a slit pore width $H=10\sigma$. The solid circles are from the simulation results (Ref. [12]).

sity. Through the numerical calculations, the diameter of a hard sphere σ was taken as the unit length. A standard Picard iteration technique was used to calculate the local density distribution $\rho(z)$.

In Fig. 1, we present the weight function $\omega(r, \rho)$ as a function the bulk density ρ . The weight function shows the strong density behaviors. Notice here that the weight function $\omega(r, \rho)$ depends only on the bulk density ρ , but not on the monomeric units N composed of a polymer fluid.

The calculated local density distributions of n -mers with $n=3$ and 20 were presented in Figs. 2 and 3, where the

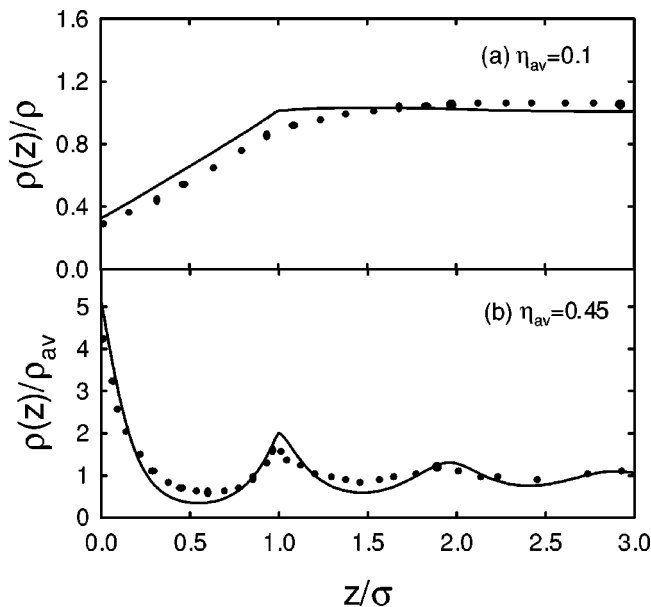


FIG. 3. Local density distributions of $n=20$ n -mers. (a) $H = 16\sigma$ and (b) $H = 10\sigma$. The solid circles are from the simulation results (Refs. [13,14]).

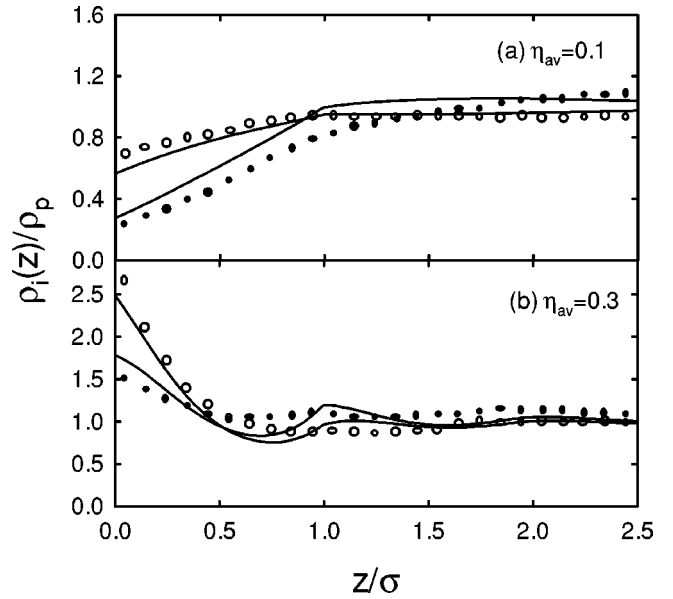


FIG. 4. Local density distributions of the end and middle segment of hard-sphere n -mers with $n=20$ ($H=16\sigma$). The solid and open circles represent the end and middle segment, respectively (Ref. [13]).

packing density of chain segments η is defined as $\eta = \pi\rho\sigma^3/6$. The average packing density η_{av} is defined as $\eta_{av} = (\pi/6H)\int_0^H \rho(z)dz$. As shown in Figs. 2 and 3, at low bulk density, the theoretical results are in excellent agree-

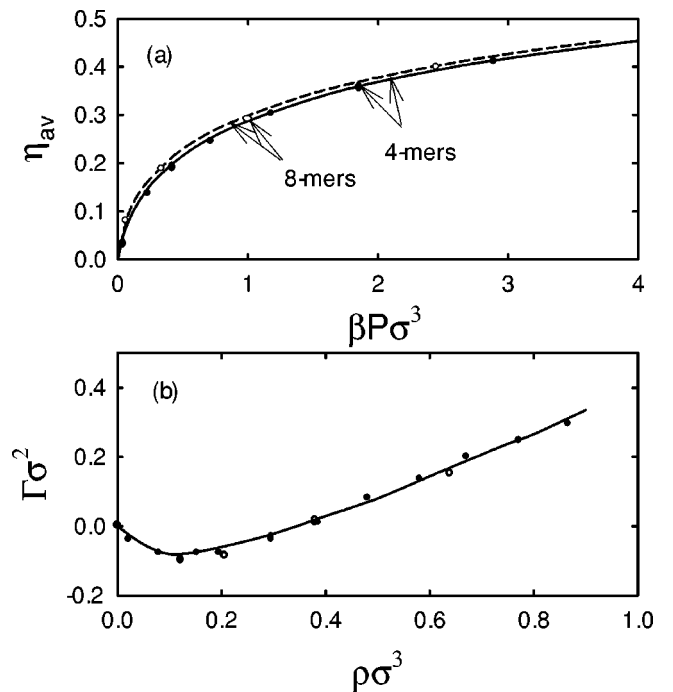


FIG. 5. (a) Adsorption isotherms of n -mers with $n=4$ and 8 in a slit pore width $H=5\sigma$. The solid and open circles are from the computer simulations (Ref. [13]). (b) Surface excess of ($n=20$)-mers near a hard wall. The open and solid circles are from the computer simulation (Refs. [13,14]) and the CMS-DF approximation of Hooper *et al.* (Ref. [15]), respectively.

ment with Monte Carlo simulations [12–14] for the local density distributions. However, the accuracy slightly deteriorates with increasing the bulk density; near a hard wall, the present approximation shows the higher density distributions compared with the computer simulation. Even though we did not display any other results [3,13] in figures, a comparison shows that the present approximation compares with those of Yu and Wu [3]. These results confirm that the DFPT based on the “coarse-grained” density yields better results than the integral equation theory. Our results also suggest that the present approximation describes the configurational entropic effects caused by the depletion of longer chains from the surfaces as compared to shorter chains very well.

The density distributions of the end and middle segment of hard-sphere n -mers with $n=20$ in a slit pore width $H=16\sigma$ were presented in Fig. 4 along with the computer simulations [13], where the segment density distribution $\rho_i(z)$ is defined as $\rho_i(z)=\xi \exp\{c_{hs}^{(1)}(z;[\rho])+c_{chain}^{(1)}(z;[\rho])\}G^i(z)G^{N+1-i}(z)$. The present approximation predicts that the density of chain ends near a hard wall is greater than the density of central beads. Once again, an excellent agreement with the computer simulations is found at low density. However, the accuracy slightly deteriorates at high densities expected from Figs. 2 and 3.

Figure 5(a) shows the adsorption isotherms of n -mers of $n=4$ and 8 in a slit pore width $H=5\sigma$. The pressure P acting on the inside faces of the two hard walls is given by βP

$=\rho(z=0)$, where $\rho(z=0)$ is the contact density at the hard wall. Figure 5(b) shows the surface excess of n -mers with $n=20$ near a hard wall, where the surface excess is defined as $\Gamma=\int_0^\infty[\rho(z)-\rho]dz$. Once again, our predictions are in good agreement with the computer simulation [14] and those from the CMS-DF approximation of Hooper *et al.* [15].

In summary, we have developed the DFPT, which was based both on the FMT and on the HWDA, to study the structural properties of nonuniform polymer melts at interfaces. The overall agreement with the computer simulation is excellent, even through the accuracy between the theoretical prediction and the computer simulation slightly deteriorates with increasing density. As a comment, the disadvantage of the present approximation is that the second-order DCF $c_{chain}^{(2)}(r,\rho)$ of the model polymers comes from other theories as well as the bridge density functional approximation proposed by Zhou [16], while the DFPT proposed by Yu and Wu [3] yields the self-consistent solutions. On the other hand, the success of the present approximation for a freely jointed tangent hard-sphere chain suggests the application of the proposed DFPT to the case of a chain-sphere mixture [3,14]. We will study this problem in the future.

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