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Simple weighted density functional approach to the structure of polymers at interfaces

Chandra N. Patra and Swapan K. Ghosh*
Theoretical Chemistry Section, RC&CD Division, Chemistry Group, Bhabha Atomic Research Centre, Mumbai 400 085, India

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A simple weighted density functional approach is employed here for predicting the structure of polymers at interfaces where the polymer molecules are modeled as freely rotating fused-hard-sphere chains with fixed bond lengths and bond angles. The approach treats the ideal gas free energy functional exactly while the excess free energy functional is evaluated using a weighted density approximation. The weight function and the bulk fluid direct correlation function required in the theory are obtained using the Denton-Ashcroft recipe and the polymer reference interaction site model integral equation theory, respectively. The calculated density profiles are shown to be in good agreement with computer simulation results.

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The liquid structure of polymer melts at interfaces is of importance in many technological applications such as lubrication, surface finishing, and liquid polymer alloys [1]. In recent years, considerable interest has grown in this area of research due to the advances in experimental measurements as well as significant progress in liquid state theoretical methods and computer simulation. Although computer simulations [2,3] have been used quite extensively for polymers near surfaces, for long chain polymers at realistic meltlike densities, they become too computationally intensive. Theoretical approaches like integral equation theory [4] and density functional theory (DFT) [5–10], on the other hand, do not suffer from such disadvantages and have, therefore, been employed in such situations.

The structure of polymer melts confined between surfaces has been studied in detail by Yethiraj and Woodward (YW) [9] through a Monte Carlo weighted density functional approach where the density profile of the polymer melt is obtained from the simulation of a single chain in a self-consistently determined field due to the rest of the molecules as well as the surfaces. The YW predictions for the density profiles for hard chains are found to be quite accurate except at very high densities, where the density profiles are found to be somewhat displaced as compared to the simulation results. The YW theory has also been applied [11] to predict the effect of attractions on the structure of freely rotating fused-hard-sphere chains confined between surfaces and the results are found to be quite comparable with computer simulations [12].

The YW theory is based on the weighted density approximation (WDA), with the specific choice of step function as the weight function, which is, therefore, independent of intermolecular interactions and polymer architecture. Subsequently, Yethiraj [10] attempted to improve the results of YW by using a more sophisticated choice of the weight function from the Curtin and Ashcroft (CA) recipe [13], using the bulk fluid direct correlation function (DCF) calculated from the polymer reference interaction site model (PRISM) [14,15] theory. The theory was found to be quite accurate for the density profiles of freely jointed tangent hard-sphere chains and freely rotating fused hard-sphere chains confined between surfaces. Since a number of choices for the weight function are readily available in liquid state theories, it would be of interest to examine the applicability of a different weight function to the case of polymers. Such an attempt has recently been made [16] by using a Denton-Ashcroft (DA) [17] weight function for freely jointed tangent hard-sphere chain models, and the results are found to be quite comparable with computer simulations. In the present work, we investigate the applicability of the DA weight function for the freely rotating fused-hard-sphere chains confined between two walls. Although the CA recipe also yields quite accurate results, the weight function calculation involves solution of a nonlinear differential equation and is much more difficult than the DA method where one has an explicit expression for the weight function in terms of the correlation functions.

In DFT of inhomogeneous fluids, the grand potential Ω is treated as a functional of the density distribution [18]. For polymers, the molecular density $\rho_M(\mathbf{R})$ is a function of the positions $\mathbf{R}=\{\mathbf{r}_i\}$ of all the N monomer sites of a polymer molecule. The grand potential $\Omega[\rho_M(\mathbf{R})]$ is defined as the Legendre transform of the Helmholtz free energy functional $F[\rho_M(\mathbf{R})]$ as

$$\Omega[\rho_M(\mathbf{R})]=F[\rho_M(\mathbf{R})]+\int[u(\mathbf{R})-\mu]\rho_M(\mathbf{R})d\mathbf{R}, \quad (1)$$

where μ is the chemical potential and $u(\mathbf{R})$ is the external potential responsible for the density inhomogeneity. The free energy $F[\rho_M]$ is expressed as the sum $F[\rho_M(\mathbf{R})]=F_{\mathrm{id}}[\rho_M(\mathbf{R})]+F_{\mathrm{ex}}[\rho(\mathbf{r})]$, with the functional $F_{\mathrm{id}}[\rho_M(\mathbf{R})]$ representing the ideal gas contribution given by the exact expression

$$F_{\mathrm{id}}[\rho_M(\mathbf{R})]=\beta^{-1}\int d\mathbf{R}\rho_M(\mathbf{R})[\ln\{\Lambda^3\rho_M(\mathbf{R})\}-1]+\int d\mathbf{R}\,V(\mathbf{R})\rho_M(\mathbf{R}), \quad (2)$$

where $\beta=(k_BT)^{-1}$, k_B is the Boltzmann constant, T is the absolute temperature, Λ is the thermal de Broglie wavelength, and $V(\mathbf{R})$ describes the internal potential generated

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*Electronic mail: skghosh@magnum.barc.ernet.in due to all the intramolecular interactions (including bonding and the long-range excluded volume). The excess free energy is treated as a functional $F_{\mathrm{ex}}[\rho]$ of the single particle average site density $\rho(\mathbf{r})$ given by

$$\rho(\mathbf{r})=\int d\mathbf{R}\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\rho_M(\mathbf{R}). \tag{3}$$

The exact functional form of $F_{\mathrm{ex}}[\rho]$ is yet unknown and hence is approximated here, within the WDA, as

$$F_{\mathrm{ex}}[\rho(\mathbf{r})]=\int d\mathbf{r}\,\rho(\mathbf{r})f(\overline{\rho(\mathbf{r})}), \tag{4}$$

where $f(\overline{\rho(\mathbf{r})})$ is the excess free energy per site of the bulk fluid evaluated at an effective site density $\overline{\rho(\mathbf{r})}$, obtained as the weighted average

$$\overline{\rho(\mathbf{r})}=\int d\mathbf{r}'\rho(\mathbf{r}')w(|\mathbf{r}-\mathbf{r}'|;\overline{\rho(\mathbf{r})}) \tag{5}$$

of the actual density distribution $\rho(\mathbf{r})$ using a suitable normalized weight function w.

The molecular density profile corresponding to a minimization of the grand potential is given by

$$\rho_M(\mathbf{R})=\zeta\exp\left[-\beta V(\mathbf{R})-\beta u(\mathbf{R})-\beta\sum_{i=1}^{N}\lambda(\mathbf{r}_i)\right], \tag{6}$$

where $\zeta\equiv\exp(\beta\mu)/\Lambda^3$ is the fugacity and $\lambda(\mathbf{r})=\delta F_{\mathrm{ex}}[\rho]/\delta\rho(\mathbf{r})$ represents an effective field that can be evaluated within the WDA as

$$\lambda(\mathbf{r})=f(\overline{\rho(\mathbf{r})})+\int d\mathbf{r}'\rho(\mathbf{r}')w(|\mathbf{r}-\mathbf{r}'|;\rho)f'(\overline{\rho(\mathbf{r}')}), \tag{7}$$

where $f'=df/d\rho$. It may be noted that for simplification we have considered the argument of the weight function to be the bulk density ρ instead of the weighted density $\overline{\rho(\mathbf{r})}$ as used in Eq. (5).

The quantity $f(\rho)$ can be taken from a suitable equation of state for polymers. In our earlier work [16], we employed the generalized Flory dimer equation of state [19] as was done by Yethiraj [10], since it was found to be quite successful for freely jointed hard chains. Following Yethiraj [10], we have also used the empirical equation of state for the present case of fused sphere chains confined between surfaces. For the weight function, we follow the DA recipe [17] which has recently been employed successfully for different types of complex fluid [17,20] as well as polymers [16], and use the approximation given by

$$w(r;\rho)=\frac{c(r;\rho)}{\hat{c}(0;\rho)}, \tag{8}$$

where $c(r;\rho)$ denotes the site-averaged DCF at the bulk density ρ and $\hat{c}(0;\rho)$ is the $k=0$ limit of its Fourier transform. It may be noted that the use of the bulk density ρ instead of $\overline{\rho(\mathbf{r})}$ as the argument of w leads to tremendous computational simplification [16,20]. The DCF $c(r;\rho)$ is obtained by solving the PRISM equation

$$\hat{h}(k)=\hat{\omega}(k)\hat{c}(k)\hat{\omega}(k)+\rho\hat{\omega}(k)\hat{c}(k)\hat{h}(k) \tag{9}$$

simultaneously with the Percus-Yevick closure [21], with $\hat{h}(k)$ being the total correlation function and $\hat{\omega}(k)$ referring to the single chain structure factor, which in the present work is obtained from a single chain Monte Carlo simulation for the freely rotating fused-hard-sphere chains.

The calculation of the density profile thus involves an iterative procedure to solve the final density equation

$$\rho(\mathbf{r})=\zeta\int d\mathbf{R}\left[\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\right]\times\exp\left[-\beta V(\mathbf{R})-\beta u(\mathbf{R})-\beta\sum_{i=1}^{N}\lambda(\mathbf{r}_i)\right], \tag{10}$$

by using a Newton-Raphson technique (described previously by YW [9]) with $V(\mathbf{R})$ obtained at each iteration through a single chain simulation in the field of the other fluid molecules and the surfaces. For the polymer melt confined between two planar hard walls as considered here, the external potential and hence also the density varies only along the perpendicular z direction, thus requiring only the planar-averaged weighted density $\overline{\rho(z)}$ and the weight function $\overline{w}(z)$ given by $\overline{\rho(z)}=\int dz'\rho(z')\overline{w}(|z-z'|;\rho)$ and $\overline{w}(z;\rho)=\int dx\int dy\,w(\mathbf{r};\rho)$, respectively, for evaluating the corresponding self-consistent effective field $\lambda(z)$. It may be noted that, while the argument used in the weight function here is the bulk density ρ, for comparison, we have also carried out calculations with a weight function involving the position-dependent weighted density but the results are almost identical in both the schemes. Hence we report here only the results obtained through the present scheme.

We have calculated the density profiles of a model polymer (N-mer) confined between two hard walls of separation $H=10\sigma$. Each polymer molecule is modeled here as fused-hard-sphere chains with fixed bond lengths l and bond angles θ and no restrictions on torsional rotations (freely rotating). To mimic the alkanes, we have chosen $l=0.4\sigma$ and $\theta=109.47°$. Beads on the same chain that are separated by four or more bonds as well as beads on different chains are assumed to interact via a hard-sphere potential.

In the present work, we have considered $N=8$ and 16, and $\rho_{\mathrm{av}}\sigma^3=0.2$, 1.0, and 1.8, where ρ_{av} is the average site density of the polymeric fluid between the two surfaces, so that we can compare our results with that of Yethiraj [9,10]. Figure 1 shows the plots of the calculated density profiles for $N=8$ using three weight functions, viz., the step function model used by YW [9], the CA scheme [13] used by Yethiraj [10], and the present scheme, along with the corresponding results obtained by direct computer simulation. The density profiles of model polymer melts are governed by competition between the single chain configurational and many chain packing entropic effects. At low densities, the chains are

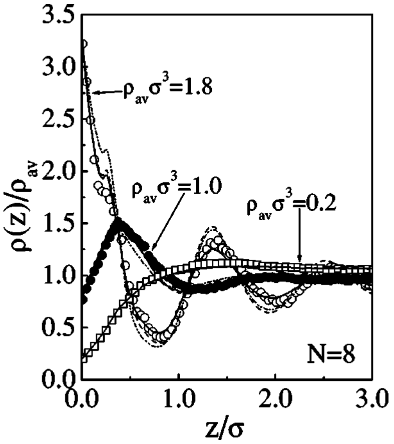

FIG. 1. Density profiles of 8-mers at $\rho_{\mathrm{av}}\sigma^3=0.2$, 1.0, and 1.8. Present work (——); YW theory [9] (-⋯-⋯); Yethiraj [10] (— — —). Circles represent Monte Carlo simulations.

found to prefer the bulk region to prevent the loss in configurational entropy for a single chain near the surface, while at higher densities, the chains pack against the surface to utilize the available free volume most efficiently. The dominance of the configurational entropic effect causes the depletion of longer chains from the surface as compared to shorter chains, as can be seen for $N=16$ in Fig. 2.

To gain insight into the success of the present WDA scheme, we have plotted the weight function $w(r)$ in Fig. 3 for $N=8$ and at the three densities $\rho_{\mathrm{av}}\sigma^3=0.2$, 1.0, and 1.8 along with the density independent step function form of $w(r)$ used by YW [9] as well as that calculated from the CA scheme [13] (at $\rho_{\mathrm{av}}\sigma^3=1.8$ only) by Yethiraj [10]. The nature and strong dependence of $w(r)$ on density indicates the importance of intermolecular interactions in such a calculation. We have also plotted the planar-averaged weight functions $\overline{w}(z)$ in Fig. 4 for different schemes corresponding to the same densities and chain lengths as in Fig. 3. The similarity between the DA and CA weight functions clearly justifies the predictions of comparable results by both these schemes. The profiles of $\overline{w}(z)$ and their dependence on density provide insight into the contributions of different regions to the overall weighted density and hence the excess free energy.

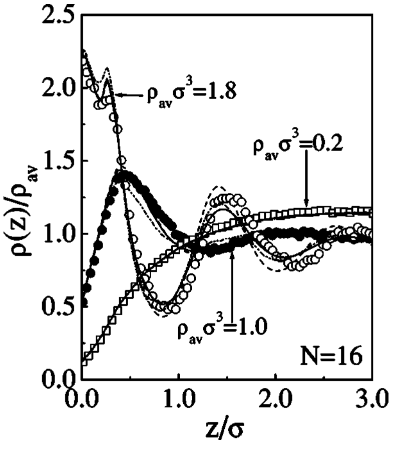

FIG. 2. Density profiles of 16-mers at $\rho_{\mathrm{av}}\sigma^3=0.2$, 1.0, and 1.8. The key is the same as in Fig. 1.

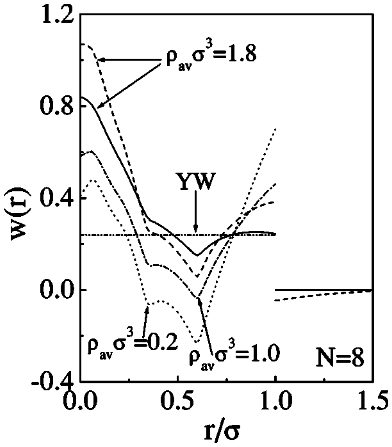

FIG. 3. Plot of the weight function $w(r)$ for 8-mers at $\rho_{\mathrm{av}}\sigma^3=0.2$, 1.0, and 1.8. Present work: $\rho_{\mathrm{av}}\sigma^3=0.2$ (· · · ·), 1.0 (—·—·—·—), 1.8 (——); YW theory (-⋯-⋯); CA recipe ($\rho_{\mathrm{av}}\sigma^3=1.8$) (— — —).

The simple weighted density functional approach proposed here is thus found to predict the density profiles of polymers at interfaces in quantitative agreement with simulations at all the average densities and chain lengths studied. The oscillations in the density profiles are also quite well reproduced by the present theory. At low density, the chains are depleted from the surface, whereas at high density, the chains pack against the surface. Entropic effects also play a dominant role in determining the effect of chain length on the overall density profiles.

The present formalism and the results can be directly applicable for the calculation of depletion-induced effective interactions [22] in colloid-polymer mixtures. The predicted preference of polymer for the bulk (at low polymer density) is reminiscent of the depletion layer near the surface of a colloidal particle. If the colloidal particles are modeled as large hard spheres, the depletion-induced interactions can be calculated from the difference of densities of the polymer

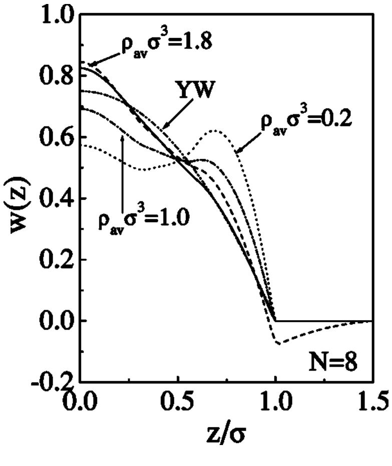

FIG. 4. Plot of the planar-averaged weight function $\overline{w}(z)$ for 8-mers at $\rho_{\mathrm{av}}\sigma^3=0.2$, 1.0, and 1.8. The key is the same as in Fig. 3.

molecules. In other words, the force between the colloidal particles immersed in polymer melts can be calculated from the present formalism.

It is highly encouraging to note that the proposed theory provides very good results just by introducing a simple weight function which takes into account the intermolecular interactions and also the molecular architecture. The important point to note is the simplicity of calculation of the weight function in the present approach as compared to the same calculation in other methods of comparable accuracy. It would be worthwhile to use a different bulk equation of state from the generalized Flory dimer equation. Also the theory can be easily extended to more realistic polymer models to include branching as well as different kinds of intermolecular potential.

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