Density functional theory for semiflexible and cyclic polyatomic fluids

Dapeng Cao and Jianzhong Wu

Department of Chemical and Environmental Engineering, University of California, Riverside, California 92521

(Received 7 April 2004; accepted 27 May 2004)

The effects of bond angle and chain stiffness on the structures of semiflexible polyatomic fluids are investigated by incorporating the bending potential into a density functional theory [Y. X. Yu and J. Z. Wu, J. Chem. Phys. 117, 2368 (2002)] that combines a modified fundamental measure theory for the excluded-volume effects and the first-order thermodynamics perturbation theory for the chain connectivity. The refined density functional theory faithfully reproduces the density profiles and conformational properties of a variety of triatomic fluids near a hard wall in which extensive Monte Carlo simulation data are available. In particular, the theory is able to capture the structures of rigid cyclic trimers where all segments are identical. The variation of local density profiles with respect to the chain length of confined polyatomic fluids is also explored. For quadratic fluids confined in slit pores, the density profile of the middle segments exhibits novel double peaks that are absent in a fully flexible chain model. In addition, the density functional theory is applied to predicting the conformational properties and adsorption behavior of heterogeneous triatomic fluids of type "ABB" mimicking surfactant molecules. The competition between surface adsorption and self-association of trimers consisting of surface active and self-binding "A" segments and neutral "B" segment is explored. © 2004 American Institute of Physics. [DOI: 10.1063/1.1774983]

I. INTRODUCTION

Density functional theory (DFT) of polyatomic fluids, pioneered by Chandler and others,1–4 has proved to be a versatile and powerful tool to represent the microscopic structures and interfacial phenomena of polymers under a variety of situations. A number of approaches have been proposed in the past decade that are able to faithfully reproduce the structural and thermodynamic properties of relatively simple models of polymeric fluids such as confined tangent hard-sphere or Lennard-Jones chains.5–11 However, applications of DFT for understanding the order-disorder phenomena in more complex molecular systems such as surfactant solutions or copolymers remain sparse, largely due to the difficulties in modeling the details of chain connectivity in surfactant-like molecules and the disparity of segments in copolymers. In this work, we intend to incorporate the bending potential into a recently proposed polymer density functional theory9,10 and extend the formulation for applications to systems containing heterogeneous polyatomic molecules.

The simplest molecular model admitting a bending potential consists of three atoms and two bonds wherein the intramolecular potential depends on the bond lengths and a bond angle, as in water or carbon dioxide. Despite its simplicity, such model is apparently relevant to practical applications, e.g., in developing more sophisticated theoretical models for water or in studying the self-assembly behavior of copolymers in supercritical carbon dioxide. With the atoms assumed to be identical hard spheres and the bond connectivity represented by a Dirac-delta function, Phan, Kierlik, and Rosinberg12 investigated the structures and conformational properties of various triatomic fluids in the vicinity of a hard wall using Monte Carlo simulations and a polymer density functional theory of Kierlik and Rosinberg.4,13,14 A very good agreement was observed between simulation results and DFT predictions for rigid triatomic fluids of different bond angles and semiflexible fluids of various bending potentials at both low and high densities. One drawback is, however, that the DFT is not self-consistent for cyclic molecules (e.g., rigid trimers at a bond angle θ0 = 60°) because it predicts different density profiles for identical sites. Alternative density functional theories complemented with single chain Monte Carlo (MC) simulations have also been proposed to account for the effect of bending potential on polymer structures. In particular, Yethiraj15 extended Curtin-Ashcroft formulation for the weighted density approximation of hard spheres combined with single-chain MC simulations to fully flexible and rigid athermal polymers using the direct correlation functions obtained from the reference polymer reference interaction site model for bulk fluids. It was found that the Curtin-Ashcroft approach improved an earlier version of the polymer density functional theory by Yethiraj and Woodward16,17 that is based on an equation of state for bulk polymeric fluids. The improvement is most significant for systems at high densities. For a fused-sphere chain model with fixed bond angles and bond lengths, the theory is in excellent agreement with simulation results for polymers near a hard wall at low and intermediate densities but overestimates the magnitude of layering at high densities.

In our previous work,9,10 we proposed a DFT for inhomogeneous mixtures of polymeric fluids by combining a modification of Rosenfeld’s fundamental measure theory15,19.
for the excluded volume effects and a first-order thermodynamic perturbation theory\textsuperscript{20} for chain connectivity. The formulation for the Helmholtz energy functional follows a similar approach to an earlier polymer density functional theory by Kierlik and Rosenberg,\textsuperscript{13} which had been applied by Phan, Kierlik, and Rosenberg\textsuperscript{12} to semiflexible trimers. However, our DFT distinguishes from the one by Kierlik and Rosenberg\textsuperscript{13} in terms of both the hard-sphere repulsion and chain connectivity. By using a modified fundamental measure theory for hard spheres, our DFT provides more accurate structure and thermodynamic properties, in particular at high density. Besides, our semipirical formulation of the chain connectivity term was inspired by Rosenfeld’s vector weighted densities; it makes the polymeric DFT not only computationally more convenient but also numerically more accurate in comparison with simulation data. By extending the Percus “trick,” we have demonstrated that the density functional theory is able to describe the nonideality of both intermolecular and intramolecular correlation functions.\textsuperscript{21} This contrast with an earlier remark made by Kierlik and Rosenberg that TPT1-type density functional theory is unable to describe the structural properties of homogeneous polymers in dilute or semidilute regimes.\textsuperscript{13} In addition, we recognized that the limitation of the self-inconsistency in Kierlik-Rosenberg theory for symmetric cyclic trimers can be avoided by taking an alternative implementation of the density functional theory for solving the density profiles. Encouraged by the excellent performance of our theory in comparison with simulation results for freely connected polymeric fluids in the bulk and under confinement, we intend to refine the formulation by including the bond-angle-dependent bending potential. This extension will allow us to address the effect of chain stiffness on conformational properties of polyatomic fluids and ultimately to investigate self-assembly and order-disorder transitions of surfactants and copolymers in the bulk and in confined geometry.

The reminder of this paper is organized as follows: In Sec. II, we recap the key equations of the polymer density functional theory and extend it for rigid and semiflexible molecules by including the bending potential and van der Waals attractions. A general procedure is outlined to apply the DFT to semiflexible polyatomic fluids. Section III compares the predictions of the DFT with MC data for rigid and flexible trimers in hard slit pores. The “calibrated” theory is then applied to predicting the structures of longer molecules and further conformational properties and the adsorption behavior of surfactantlike molecules. Finally, Sec. IV concludes with some remarks for future work.

II. THEORY

A. Density functional theory for rigid trimers

1. Bonding potential of rigid trimers

We consider first rigid, tangentially connected trimers consisting of spherical hard segments where the bond length is equal to the segment diameter $\sigma$ and the bond angle is fixed at $\theta_0$. As discussed later, similar formulation is applicable to multisegmental rigid or semiflexible polymers and polyatomic fluids. The intramolecular potential for the chain connectivity is represented by

$$V_{\beta}(\mathbf{R}) = V_{BL}(\mathbf{r}_2 - \mathbf{r}_1) + V_{BL}(\mathbf{r}_3 - \mathbf{r}_2) + V_{BA}(\theta_{123}),$$

where the subscript BL denotes the stretching potentials related to the bond length, the subscript BA denotes the bending potential related to the bond angle, and the subscript $B$ stands for the total bonding potential. The composite vector $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ consists of a set of coordinates indicating the positions of the segments in a triatomic molecule. For tangentially connected rigid trimers, the total bonding potential satisfies

$$\exp[-\beta V_{\beta}(\mathbf{R})] \approx \delta(|\mathbf{r}_2 - \mathbf{r}_1| - \sigma) \delta(|\mathbf{r}_3 - \mathbf{r}_2| - \sigma) \times \delta(\theta_{123} - \theta_0),$$

where $\beta = 1/kT$ and $\delta(r)$ is the Dirac delta function. Equation (2) states that the probability density of a rigid trimer with a configuration $\mathbf{R}$ is proportional to the Boltzmann factor $\exp[-\beta V_{\beta}(\mathbf{R})]$. Based on the normalization condition for the probability distribution of segments,

$$\left(1/V\right) \int \exp[-\beta V_{\beta}(\mathbf{R})] d\mathbf{R} = 1,$$

we can fix the proportionality constant in Eq. (2),

$$\exp[-\beta V_{\beta}(\mathbf{R})] = \frac{\delta(|\mathbf{r}_2 - \mathbf{r}_1| - \sigma)}{4\pi\sigma^2} \frac{\delta(|\mathbf{r}_3 - \mathbf{r}_2| - \sigma)}{4\pi\sigma^2} \frac{\delta(\theta_{123} - \theta_0)}{(1/2)\sin \theta_0},$$

$$\theta_0 \in (0, \pi).$$

Equation (4) provides a starting point for formulating the Helmholtz energy functional of rigid triatomic fluids.

2. Helmholtz free energy functional

The central idea of a density functional theory is that given a grand potential functional $\Omega[\rho_M(\mathbf{R})]$, the equilibrium density profile $\rho_M(\mathbf{R})$ can be solved from the stationary condition

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

thereby all thermodynamic properties can be evaluated following statistical thermodynamic relations. For a polymeric fluid, the grand potential is related to the Helmholtz energy functional via the Legendre transformation

$$\Omega[\rho_M(\mathbf{R})] = F[\rho_M(\mathbf{R})] + \int \left[ \psi_M(\mathbf{R}) - \mu_M \right] \rho_M(\mathbf{R}) d\mathbf{R},$$

where $\rho_M(\mathbf{R})$ is a multidimensional density profile depending on the positions of all segments of the polymeric molecule. The molecular density profile $\rho_M(\mathbf{R})$ is related to the segmental densities by

$$\rho(\mathbf{r}) = \sum_{i=1}^{M} \rho_M(\mathbf{r}) = \sum_{i=1}^{M} \int d\mathbf{R} \delta(\mathbf{r} - \mathbf{r}_i) \rho_M(\mathbf{R}),$$
where \( \rho(r) \) is the total segmental density and \( \rho_{ai}(r) \) is the local density of segment \( i \). For a rigid trimer, \( M \) is equal to 3 and \( dR = dr_1 dr_2 dr_3 \) stands for a set of differential volumes. In Eq. (6), \( \mu_M \) is the chemical potential of the polymer chain and \( \psi_M(R) \) is the external potential exerting on individual segments.

The Helmholtz energy functional \( F[\rho_M(R)] \) is conventionally expressed as an ideal contribution corresponding to that for a system of ideal chains that interact only through bonding potentials and an excess part taking into account both nonbonded intermolecular and intramolecular interactions:

\[
F[\rho_M(R)] = F_{id}[\rho_M(R)] + F_{ex}[\rho_M(R)].
\]  
(8)

For polymers with only bonding potentials, the Helmholtz energy is known exactly,

\[
\beta F_{id}[\rho_M(R)] = \int dR \rho_M(R) \left[ \ln \rho_M(R) - 1 \right] + \beta \int dR \rho_M(R) V_B(R).
\]  
(9)

In addition to the direct nonbonded intersegmental interactions, the excess part of the Helmholtz energy functional accounts for the influence of the bond connectivity on intersegmental correlations. For simplicity, here we consider only the excluded volume effects represented by hard spheres. Additional formulations for other potentials have also been developed.\(^{22-24}\)

As in our earlier work for flexible hard-sphere chains,\(^{9,10}\) the excess Helmholtz energy functional is represented by

\[
\beta F_{ex}[\rho(R)] = \int dr \left\{ \phi_{hs}[n_{\alpha}(r)] + \phi_{\text{chain}}[n_{\alpha}(r)] \right\},
\]  
(10)

where \( n_{\alpha}(r) \) with \( \alpha = 0, 1, 2, 3, V_1, V_2 \) are Rosenfeld’s weighted densities,\(^{9,21}\) and \( \phi_{hs}[n_{\alpha}(r)] \) and \( \phi_{\text{chain}}[n_{\alpha}(r)] \) are, respectively, the excess Helmholtz free energy densities due to the hard-sphere repulsion and the effect of chain connectivity on the inter-segmental correlations. Note that the second term on the right-hand side of Eq. (10) arises from the indirect hard-sphere interactions due to the chain connectivity. This term is entirely different from the Helmholtz energy functional for an ideal chain as shown in Eq. (9) where the direct bonding potentials are explicitly included. Equation (10) implies that the effect of chain connectivity on intermolecular correlations can be effectively accounted for by using only the segmental densities.

According to the modified fundamental measure theory, the excess Helmholtz energy density due to the hard-sphere repulsion includes a scalar and a vector contribution,

\[
\Phi_{hs}^S[n_{\alpha}(r)] = \phi_{hs}^S[n_{\alpha}(r)] + \phi_{hs}^V[n_{\alpha}(r)],
\]  
(11)

where the scalar part is equivalent to that from the Boublik-Mansoori-Carnahan-Starling-Leland equation of state.\(^{25}\)

\[
\Phi_{hs}^S[n_{\alpha}(r)] = -n_0 \ln(1 - n_3) + \frac{n_1 n_2}{1 - n_3} + \frac{n_3^3 \ln(1 - n_3)}{36 \pi n_3^3} + \frac{n_2^2}{36 \pi n_3(1 - n_3)^2},
\]  
(12a)

and the vector part takes into account the gradients of local inhomogeneity.

\[
\Phi_{hs}^V[n_{\alpha}(r)] = \frac{n_1 n_2 n_3 V}{12 \pi n_3^3} \ln(1 - n_3) - \frac{n_2 n_3 n_4 n_5}{12 \pi n_3^3 (1 - n_3)^2},
\]  
(12b)

An extension of the first-order perturbation theory for chain connectivity for a bulk system to inhomogeneous systems gives\(^{9,10}\)

\[
\Phi_{\text{chain}}[n_{\alpha}(r)] = \frac{1 - M}{M} n_0 \xi \ln y_{hs}(\sigma, n_{\alpha}),
\]  
(13)

where \( \xi = 1 - n_1 \cdot n_2 / n_3 \) stands for an inhomogeneous factor and \( y_{hs}(\sigma, n_{\alpha}) \) is the contact value of the cavity correlation function between segments given by

\[
y_{hs}(\sigma, n_{\alpha}) = \frac{1}{1 - n_3} + \frac{n_2 \xi \sigma}{4(1 - n_3)^2} + \frac{n_2^2 \xi \sigma}{72(1 - n_3)^3}.
\]  
(14)

Equation (13) distinguishes from earlier versions of polymeric DFT including the one by Kierlik and Rosinberg\(^{13}\) that require the correlation function of a polymeric fluid as an input. We have demonstrated in our previous work that in comparison with simulation results, Eq. (13) is more accurate than previous versions of DFT.\(^{9,10}\)

### 3. Euler-Lagrange equations

Minimization of the grand potential with respect to the density profiles, namely, Eqs. (5) and (6), gives the Euler-Lagrange equation

\[
\rho_M(R) = \exp \left[ \beta \mu_M - \beta V_B(R) - \beta \sum_{i=1}^{M} \lambda_i(r_i) \right],
\]  
(15)

where the self-consistent potential \( \lambda_i(r_i) \) denotes the excess Helmholtz free energy and external potential \( \varphi_i(r_i) \),

\[
\lambda_i(r_i) = \frac{\delta F_{ex}}{\delta \rho(r_i)} + \varphi_i(r_i).
\]  
(16)

Combination of Eqs. (7), (15), and (16) yields the segmental densities \( \rho_{ai}(r) \),

\[
\rho_{ai}(r) = \int dR \delta(r - r_i) \exp \left[ \beta \mu_M - \beta V_B(R) - \beta \sum_{j=1}^{M} \lambda_j(r_j) \right].
\]  
(17)

Subsequently, the average segment density of rigid trimer chains is represented by
\[ \rho(r) = \exp(\beta \mu_M) \int dR \sum_{i=1}^{M} \delta(r - r_i) \times \exp \left[ -\beta V_b(R) - \beta \sum_{j=1}^{M} \lambda_j(r_j) \right]. \]  

(18)

**4. Density profiles of rigid trimers in slit pores**

For rigid trimers in a hard slit pore, the external potential for each segment is given by

\[ \varphi_i(z) = \begin{cases} \infty, & z < 0 \text{ or } z > H \\ 0, & \text{otherwise,} \end{cases} \]  

(19)

where \( z \) is the perpendicular distance from the wall and \( H \) is the pore width. For systems with the density distribution changing only in the \( z \) direction, \( \rho(r) \) becomes \( \rho(z) \). Thus, we can derive the density profile of the end segment, \( \rho_1(z) \), from Eq. (17),

\[ \rho_1(z) = \frac{\exp[\beta \mu_M - \lambda(z)]}{4 \pi \sigma} \times \int_{z-\sigma}^{z+\sigma} \exp[-\lambda(z_1)] dz_1 \times \int_0^{2\pi} \exp[-\lambda[z_3(z_2, z_1), \theta_0, \varphi')] d\varphi'. \]  

(20)

where

\[ z_3(z_2, z_1, \theta_0, \varphi') = z + \frac{1 - \cos \theta_0}{\sigma^2 - (z_2 - z)^2}, \]  

(21)

and that for the middle segment, \( \rho_2(z) \), is

\[ \rho_2(z) = \frac{\exp[\beta \mu_M - \lambda(z)]}{4 \pi \sigma} \times \int_{z-\sigma}^{z+\sigma} \exp[-\lambda(z_1)] dz_1 \times \int_0^{2\pi} \exp[-\lambda[z_3'(z_1, \theta_0, \varphi')] d\varphi'. \]  

(22)

where

\[ z_3'(z_1, \theta_0, \varphi') = z_1 + \frac{1 - \cos \theta_0}{\sigma^2 - (z_1 - z)^2}. \]  

(23)

In Eqs. (20) and (22), the chemical potential of the chain molecule can be directly obtained from the equation of state for the corresponding bulk fluid26

\[ \beta \mu_M = \ln \rho_M + M \beta \mu_{M}^{bs}(\rho_b) + (1 - M) \left[ \ln \rho_{M}^{bs}(\sigma) + \rho_b \frac{\partial \ln \rho_{M}^{bs}(\sigma)}{\partial \rho_b} \right], \]  

(24)

where \( \rho_b = M \rho_M \) is the bulk densities of segments and \( \mu_{M}^{bs} \) is the excess chemical potential of corresponding hard spheres given by the Carnahan-Starling equation of state.25

We note that in addition to the different expressions for the excess Helmholtz energy functionals due to hard-sphere repulsion and chain connectivity, our implementation of the density functional theory is also different from that given by Phan, Kierlik, and Rosinberg.12 Instead of calculating the two-point density profiles which leads to the self-inconsistency problems for cyclic trimers, we evaluate the segmental densities directly using Eqs. (20) and (22). Because the bonding constraints are imposed exactly, our approach yields identical density profiles for equivalent segments in a cyclic polymer.

**B. Extension to flexible trimers in a hard-slit pore**

In a rigid chain model, the bond angles are fixed and the bending potential is represented by a Dirac delta function. For semiflexible trimers, Phan, Kierlik, and Rosinberg expressed the bond-angle bending potential as12

\[ U(\theta) = \begin{cases} \epsilon [1 - \cos(\theta - \theta_0)] & \text{if } \theta \geq \pi/3 \\ \infty, & \text{otherwise,} \end{cases} \]  

(25)

where \( \epsilon \) stands for a bending energy. In this case, the intramolecular Boltzmann factor is given by

\[ \exp[-\beta V_b(R)] = \frac{\delta(z_2 - r - \sigma) \delta(z_3 - r - \sigma)}{4 \pi \sigma^2} \times \frac{\exp[-\beta U(\theta)]}{(1/2) \int_0^{2\pi} \exp[-\beta U(\theta)] \sin \theta d\theta}. \]  

(26)

In writing Eq. (26), we assume that the bond length remains fixed and equal to the hard-sphere diameter. The corresponding equations for solving the end- and middle-segment density profiles become

\[ \rho_1(z) = \frac{\exp[\beta \mu_M - \lambda(z)]}{4 \pi \sigma \int_0^{2\pi} \exp[-\beta U(\theta)] \sin \theta d\theta} \times \int_{z-\sigma}^{z+\sigma} \exp[-\lambda(z_1)] dz_1 \times \int_0^{2\pi} \exp[-\lambda[z_3'(z_1, \theta_0, \varphi')] d\varphi'. \]  

(27)

and

\[ \rho_2(z) = \frac{\exp[\beta \mu_M - \lambda(z)]}{4 \pi \sigma \int_0^{2\pi} \exp[-\beta U(\theta)] \sin \theta d\theta} \times \int_{z-\sigma}^{z+\sigma} \exp[-\lambda(z_1)] dz_1 \times \int_0^{2\pi} \exp[-\lambda[z_3'(z_1, \theta_0, \varphi')] d\varphi'. \]  

(28)
where \( z_3(z, z_2, \theta, \varphi') \) and \( z'_3(z, z_1, \theta, \varphi') \) are the same as those appeared in Eqs. (21) and (23). Within the framework of the first-order perturbation theory, the bending potential has no influence on the equation of state and thus the chemical potential of trimers is still given by Eq. (24).

C. Polymeric fluids

Extension of the above formulations for multisegmental rigid or semiflexible polymeric fluids is straightforward. In general, the bonding potential can be expressed as

\[
V_B(R) = \sum_{i=1}^{M-1} V_{BL}(|r_{i+1} - r_i|) + \sum_{i=2}^{M-1} V_{BA}(\theta_{i-1,i,i+1}),
\]

(29)

where \( M \) denotes the number of segments for each chain, \( R \) is a set of coordinates describing the segmental positions, and \( \theta_{i-1,i,i+1} \) is the bonding angle formed by three consecutive segments indexed by \( i-1, i, i+1 \). For a rigid tangential polymer with fixed bond angles and bond lengths, the intramolecular Boltzmann factor satisfies

\[
\exp[-\beta V_B(R)] = \prod_{i=1}^{M-1} \delta(|r_{i+1} - r_i| - \sigma) \times \prod_{i=2}^{M-1} \delta(\theta_{i-1,i,i+1} - \theta_0).
\]

(30)

According to the normalization condition [i.e., Eq. (3)], the proportionality constant can be fixed and Eq. (30) becomes

\[
\exp[-\beta V_B(R)] = \prod_{i=1}^{M} \frac{\delta(|r_{i+1} - r_i| - \sigma)}{4\pi \sigma^2} \times \prod_{i=2}^{M-1} \frac{\delta(\theta_{i-1,i,i+1} - \theta_0)}{(1/2) \sin \theta_0}.
\]

(31)

In a slit geometry, the density profiles of segment \( i \) can be derived from Eqs. (8) and (15),

\[
\rho_{\text{m}}(z_i) = \frac{\exp(\beta \mu_M)}{2\sigma} \int_{z_i - \sigma}^{z_i + \sigma} \exp[-\lambda(z_{i+1})] \times G_L(z_i, z_{i+1})G_R(z_i, z_{i+1})dz_{i+1},
\]

(32)

where \( G_L(z_i, z_{i+1}) \) is the left recursive function and \( G_R(z_i, z_{i+1}) \) is the right recursive function, given by

\[
G_L(z_i, z_{i+1}) = \begin{cases} 1, & i = 1 \\ \frac{1}{2\pi} \int_0^{2\pi} \exp[-\lambda(z_{i-1}(z_i, z_{i+1}, \theta_0, \varphi'))]G_L(z_{i-1}, z_i)d\varphi', & i \geq 2, \end{cases}
\]

(33)

\[
G_R(z_i, z_{i+1}) = \begin{cases} 1, & i = M - 1 \\ \frac{1}{2\pi} \int_0^{2\pi} \exp[-\lambda(z_{i+2}(z_i, z_{i+1}, \theta_0, \varphi'))]G_R(z_{i+1}, z_{i+2})d\varphi', & i < M - 1, \end{cases}
\]

(34)

where

\[
z_{i-1}(z_i, z_{i+1}, \theta_0, \varphi') = z_{i+1} + (1 - \cos \theta_0)(z_i - z_{i+1}) - \sin \theta_0 \cos \varphi' \sqrt{\sigma^2 - (z_i - z_{i+1})^2},
\]

(35)

\[
z_{i+2}(z_i, z_{i+1}, \theta_0, \varphi') = z_i + (1 - \cos \theta_0)(z_{i+1} - z_i) - \sin \theta_0 \cos \varphi' \sqrt{\sigma^2 - (z_{i+1} - z_i)^2}.
\]

(36)

Similar expressions can be written for semiflexible polymers. Compared with the recurrence relations for a freely connected polymeric model, the left and right recursive functions for a rigid or semiflexible polymeric fluid are computationally much more intensive. For semiflexible polymers that entail a bending potential, the computing time is an exponential rather than a linear function of the chain length \( M \). Further-more, unlike the recurrence relations for freely connected polymeric chains, there is no symmetry between the left and right recursive functions.

D. A primitive model for surfactants

A minimum molecular model for surfactants involves two parts, one adores surface and the other prefers a bulk solution. In comparison with polymers, surfactant molecules have relatively small molecular weight and their properties are often sensitive to the stiffness of the polyatomic backbone. In this work, rigid and semiflexible tangentially connected trimers, designated as “ABB,” are used as a simple representation of surfactants. Within this framework, the density functional theory may be used to illustrate the effect of chain stiffness on surface structures and the competition between surface adsorption and self-aggregation. We assume that the head group “A” is surface active, i.e., it binds to a surface by a square-well (SW) potential
Correspondingly, the Euler-Lagrange equation becomes

$$\varphi_{\text{at}}(z) = \begin{cases} -\epsilon, & 0 < z < w \\ 0, & \text{otherwise,} \end{cases}$$

(37)

where \(\epsilon\) stands for an attractive energy and \(w\) is the width of the potential well assumed to be \(w = \sigma/4\). The remaining middle and end segments “BB” are assumed to be neutral, i.e., no attraction to the wall. We assume further that the interactions between A and B segments can also be represented by a similar SW potential

$$\varphi_{ij}(r) = \begin{cases} -\epsilon_{ij}, & \sigma \leq r \leq \gamma \sigma \\ 0, & r > \gamma \sigma, \end{cases}$$

(38)

where \(\gamma\) is the width of the attractive well assumed to be \(\gamma = 1.2\) and \(\epsilon_{ij}\) is the well depth.

According to the mean-field approximation for the short-range attractions, the excess Helmholtz energy functional can be rewritten as

$$\beta F_{\text{ex}}[\rho(r)] = \int dr \left[ \phi_{\text{fs}}[\rho_a(r)] + \phi_{\text{chain}}[\rho_a(r)] \right] + \beta F_{\text{ex}}^{\text{att}},$$

(39)

where \(\phi_{\text{fs}}\) and \(\phi_{\text{chain}}\) are the same as those given in Eqs. (12) and (13), and

$$\beta F_{\text{ex}}^{\text{att}} = \frac{1}{2} \int d|r|| \rho_{ij}(r) \rho_{ij}(r) \beta u_{ij}^{\text{att}}(r-r').$$

(40)

Correspondingly, the Euler-Lagrange equation becomes

$$\rho_{\text{M}}(R) = \exp \left[ \frac{\beta \mu_{\text{M}} - \beta V_{\text{B}}(R) - \beta \sum_{j=1}^{M_A} \lambda_{Aj}(r_j)}{4 \pi \sigma} \right]$$

$$\times \int_{z-\sigma}^{z+\sigma} \exp \left[ -\lambda_{B1}(z_2) \right] dz_2 \times \int_{0}^{2\pi} \exp \left[ -\lambda_{B2}(z_1, z_2, \theta_0, \phi') \right] d\phi',$$

(47)

$$\rho_{B1}(z) = \frac{\exp \left[ \frac{\beta \mu_{\text{M}} - \lambda_{B1}(z)}{4 \pi \sigma} \right]}{4 \pi \sigma}$$

$$\times \int_{z-\sigma}^{z+\sigma} \exp \left[ -\lambda_{A}(z_1) \right] dz_1 \times \int_{0}^{2\pi} \exp \left[ -\lambda_{B2}(z_1, z_2, \theta_0, \phi') \right] d\phi',$$

(48)

$$\rho_{B2}(z) = \frac{\exp \left[ \frac{\beta \mu_{\text{M}} - \lambda_{B2}(z)}{4 \pi \sigma} \right]}{4 \pi \sigma}$$

$$\times \int_{z-\sigma}^{z+\sigma} \exp \left[ -\lambda_{B1}(z_2) \right] dz_2 \times \int_{0}^{2\pi} \exp \left[ -\lambda_{A}(z_1, z_2, \theta_0, \phi') \right] d\phi',$$

(49)

Near a planar surface, the density varies only in the perpendicular direction (z) and the local densities are

$$\rho_{A}(z) = \frac{\exp \left[ \frac{\beta \mu_{\text{M}} - \lambda_{A}(z)}{4 \pi \sigma} \right]}{4 \pi \sigma}$$

$$\times \int_{z-\sigma}^{z+\sigma} \exp \left[ -\lambda_{B1}(z_2) \right] dz_2 \times \int_{0}^{2\pi} \exp \left[ -\lambda_{B2}(z_1, z_2, \theta_0, \phi') \right] d\phi',$$

(47)

$$\rho_{B1}(z) = \frac{\exp \left[ \frac{\beta \mu_{\text{M}} - \lambda_{B1}(z)}{4 \pi \sigma} \right]}{4 \pi \sigma}$$

$$\times \int_{z-\sigma}^{z+\sigma} \exp \left[ -\lambda_{A}(z_1) \right] dz_1 \times \int_{0}^{2\pi} \exp \left[ -\lambda_{B2}(z_1, z_2, \theta_0, \phi') \right] d\phi',$$

(48)

$$\rho_{B2}(z) = \frac{\exp \left[ \frac{\beta \mu_{\text{M}} - \lambda_{B2}(z)}{4 \pi \sigma} \right]}{4 \pi \sigma}$$

$$\times \int_{z-\sigma}^{z+\sigma} \exp \left[ -\lambda_{B1}(z_2) \right] dz_2 \times \int_{0}^{2\pi} \exp \left[ -\lambda_{A}(z_1, z_2, \theta_0, \phi') \right] d\phi',$$

(49)

where “B1” stands for the middle segment and “B2” for the end segment, \(z_1, z_1'\) are the same as those appeared in Eqs. (21) and (23). Equations (39) and (47)–(49) allow us to investigate the density distributions of self-associating and inert segments near the surface at different bending potentials and surface attractions. Apparently, similar formulation can be written for copolymers or longer heterogeneous polyatomic molecules.
III. ILLUSTRATIVE RESULTS

A. Nonlinear rigid trimers

We first test the performance of the refined density functional theory with simulation results for rigid and semiflexible trimers that have been reported before. Figure 1 depicts the end and middle site reduced density profiles for rigid trimers in a slit pore calculated from DFT and from MC simulation\(^{12}\) at the total packing fractions equal to \(\eta=0.1\) and 0.3. Here the reduced densities \(\rho_1^*(z)\) and \(\rho_2^*(z)\) are normalized to the corresponding average molecular density within the pore. Because the end site has less restriction on the configurational orientations than the middle site, the contact value of \(\rho_1^*(z)\) is always greater than that for \(\rho_2^*(z)\). For both densities, the accumulation of end segments near the surface becomes more apparent as the bond angle increases. While the end-site density at contact increases with the bond angle, the contact value of the middle-site density decreases. At low density (\(\eta=0.1\)), the middle-site density profiles exhibit a peak at \(z/\sigma=1\) for all cases, signaling that the middle site is depleted by the wall beyond this point. At higher density (\(\eta=0.3\)), in addition to the peak of the middle site appearing at \(z/\sigma=1\), some minor peaks and shoulders arise very close to the wall (\(z/\sigma=0-1\)). Apparently, the density functional theory captures all the details of the end and middle density profiles quantitatively.

It is worthwhile mentioning that when the bond angle is equal to 60°, the rigid trimers become symmetric cyclic. In this case, all segments are indistinguishable therefore the density profiles of middle and end sites become identical. This feature is faithfully reproduced by our density functional calculations. However, Phan, Kierlik and Rosinberg\(^2\) showed that the values of \(\rho_1^*(z)\) and \(\rho_2^*(z)\) are different at \(z=0\) for \(\theta_0=60°\), which was argued to be attributed to the asymmetric treatment of two-point density profiles.

B. Semiflexible trimers

A similar comparison is made for semiflexible trimers in slit pores. Figure 2 illustrates the local segment density profiles in a hard slit from the density functional theory and simulations at two packing fractions \(\eta=0.1\) and 0.3. When the reduced bending energy is \(E^b=0\), the trimer becomes fully flexible, i.e., a freely jointed triatomic chain. With the increase of the bending energy, the chain becomes stiffer and approaches the limit of rigid chains as discussed in the preceding section. For the conditions considered in this figure, the bending energy has only negligible effects on the middle- and end-segment density profiles. Understandably, this is not true for all cases, in particular for those with smaller bond angles (e.g., 60°). In general, the contact value of the end-site density should increase with the chain stiffness while opposite is true for the middle segment (see Fig. 3).

C. Effect of chain length: rigid quadatomic chains

We find that application of DFT for rigid or semiflexible chains becomes extremely time consuming as the number of segments increase. To minimize computational effort, we consider here only rigid quadatomic molecules. Nevertheless, a comparison with similar results for rigid trimers may yield some insights into the effect of chain length on the structure of polyatomic fluids. Figure 4 shows the end- and middle-segment density profiles of the rigid quadrimer at three bond angles and two different packing fractions \(\eta=0.1\) and 0.3. As for the trimers the contact value of the end-segment density is greater than that for the middle-site den-
Interestingly, the overall density profile for the end segment of quardimers is very similar to that for the trimers, which implies that the chain length has only minor effects. However, the middle-segment density profiles for the trimers and quardimers are noticeably different. For quardimers, the middle-segment density profiles exhibit double peaks approximately at the positions $z/\sigma = 1$ and 2 for the cases of bond angle equal to 150°, and these peaks are merging together as the bond angle approaches 60°. At $\eta = 0.3$ and $\theta_0 = 150°$, a third peak and a shallow shoulder appear at positions of $z/\sigma = 2.5$ and 0.5, respectively. These peaks reflect the rigid bond angles of quardimers that do not show up for freely connected polymeric chains where the chain stiffness is completely neglected.  

The difference in mid-segment density profiles between trimers and quardimers is not because the chain length has more influence on the middle segments; instead, it arises from the fact that the quardimers have two middle segments bonded in fixed angles. Interestingly, the density profiles of rigid trimers and quardimer share remarkable similarity at high densities. In this case, the fluid structure is mainly determined by the packing effect. At $\theta_0 = 60°$, there is no sym-

![FIG. 2. Same as Fig. 1 but for semiflexible trimers.](image)

![FIG. 3. The microscopic structures of semiflexible trimers with different bending potentials in a hard-slit pore. Here the bond angle is $\theta_0 = 60°$.](image)
metry for rigid quadrimers thereby the density profiles of end and middle sites are expected to be different.

D. “ABB-type” surfactants near a surface

We now apply the density functional theory to explore the effect of chain stiffness on surface structure and the competition between surface adsorption and self-aggregation between surfactant molecules.

We consider first the effect of self-association on the adsorption of surfactant to a neutral surface, i.e., the wall applies attraction neither to A nor to B segments. Figure 5 depicts the segmental density profiles of rigid ABB trimers near a neutral surface with the bond angle fixed at $\theta_0 = 120^\circ$. As the attraction between segments A and A increases with all other interactions unchanged, the contact value of the reduced segmental density for the A segments progressively drops. While the middle-segment density B1 also falls slightly, the contact density of the end segment B2 increases with the association energy between A segments. This implies that at high packing fractions, the overall density near the surface is insensitive to the self-association energy. Apparently, with the increase in the interaction between A segments, they tend to aggregate in the bulk while the other end segment B2 tends to fill the gap.

Figure 6 shows the local-segmental density profiles of ABB trimers at different bond angles and packing fractions. For simplicity, we assume that B1 and B2 are hard spheres and attraction applies only between A segments and the wall. At $\theta_0 = 60^\circ$, the trimer becomes a cyclic molecule and the two B segments become equivalent. As for the athermal trimers, the DFT predicts identical density profiles for the segments B1 and B2 which become equivalent in a symmetric rigid trimer. However, the different attractive energies between the A and B segments lead to the different density profiles near the surface. The discontinuity for the density profile of A segment is induced by the surface force represented by the square-well potential. At other bond angles, the ABB trimer exhibits different segmental density profiles for different segments, with the A segments close to the wall followed by the middle B segment and then end B segment. In this case, all molecules are oriented toward the surface in the direction of ABB, resembling the structure of a self-assembled monolayer. The positions of peaks in the density profiles increases as the bond angle becomes larger, i.e., the molecules are more stretched. Because of stronger excluded volume effects, these peaks become less distinctive as the density increases.
Figure 7 shows the adsorption isotherms of ABB trimers at different wall attractions. The surface excess $\Gamma$ is defined as

$$\Gamma = \int_0^\infty [\rho(z) - \rho_b]dz,$$

where $\rho_b$ is the bulk density. As expected, the amount of adsorption increases monotonically with the interaction energy between the molecular head and the wall. At $\epsilon_{AW}^* = 5.0$, a Langmuir-type monolayer isotherm is observed. At lower surface energy ($\epsilon_{AW}^* = 2.0$), however, the adsorption approximately follows the Henry’s law where a linear correlation between the surface density and bulk density can be obtained. As the surface energy is further decreased ($\epsilon_{AW}^* = 1.0$), the surfactant molecules are depleted from the surface at low bulk densities and a negative surface excess is predicted. Such depletion is induced by attractions between surfactant molecules in the bulk. Qualitatively, all these predictions are consistent with experimental observations.27

IV. CONCLUSIONS

We have extended our previous work for the density functional theory of freely jointed chains to include the bending potentials arising from the variation of the bond angles. A general formulation is also developed to represent the Helmholtz energy functionals of heterogeneous polyatomic fluids and copolymers that explicitly take into account the chain stiffness. In comparison with simulation results for rigid and semiflexible trimers reported by others, the refined density functional theory is able to capture the effect of bond stiffness on the inhomogeneous structures quantitatively at a variety of conditions. In particular, the present density functional theory faithfully reproduces the identical density profiles for equivalent segments as in a symmetric cyclic trimer. We find that the chain stiffness has a major effect on the microscopic structures of short chains near a surface. Regrettably, it appears that because of the lost of symmetry in the left and right propagator functions, application of the DFT for long semiflexible polyatomic chains is computationally intensive. Such difficulty might be overcome by using Monte Carlo simulation for the multidimensional integrations appeared in the evaluation of the density profiles.28

We have also explored the applicability of the refined DFT to surface behavior of ABB trimers mimicking surfactant molecules. As observed in experiments, the DFT predicts that the self-association of surfactant molecules minimizes the adsorption in a neutral surface. Conversely, a strong surface attraction leads to the alignment of surfactant molecules in which the local structure is highly sensitive to the chain configuration such as bond length and angle. Such information is potentially useful for understanding the microscopic details of self-assembled monolayers. We find that the
adsorption isotherm at a strongly attractive surface exhibits Langmuir-like behavior but a weakly attractive surface may lead to negative adsorption. Recently, TPT1-type density functional theory has been applied to represent a variety of order-disorder phase transitions in surfactant solutions that involve micelles, lamellas, vesicles, and hexagonal phases.\textsuperscript{29–36} The density functional theory at least qualitatively represents both phase diagrams and interfacial structures of surfactant systems. With a more accurate Helmholtz energy functionals as proposed in this work, application of the polymeric density functional theory for more complicated systems appears very promising.

ACKNOWLEDGMENTS

The authors wish to dedicate this work to Professor David Chandler on the occasion of his 60th birthday. The research was supported by the National Science Foundation (Grant Nos. CTS0406100 and CTS0340948). D.C. is thankful to Zhidong Li for insightful discussions.