Density-functional theory and Monte Carlo simulation for the surface structure and correlation functions of freely jointed Lennard-Jones polymeric fluids

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We present a nonlocal density-functional theory of polymeric fluids consisting of freely jointed Lennard-Jones chains with explicit consideration of the segment size, van der Waals attraction, and structural correlations due to chain connectivity. The excess Helmholtz energy functional is derived from a modified fundamental measure theory for the short-ranged repulsion and the first-order thermodynamic perturbation theory for chain connectivity. The contribution of the long-ranged attraction to the Helmholtz energy functional is taken into account using a quadratic density expansion with the direct correlation function obtained from the first-order mean-spherical approximation. The numerical performance of the density-functional theory is compared well with the simulation results from this work as well as those from the literature for the segment-level density profiles and correlation functions of Lennard-Jones chains in slit pores, near isolated nanoparticles, or in bulk. © 2005 American Institute of Physics. [DOI: 10.1063/1.1886685]

I. INTRODUCTION

Understanding the segment-level structure of polymeric fluids has been a major thrust of soft-matter science due to its close connection to the macroscopic/mesoscopic properties of polymeric materials as encountered in numerous industrial applications such as surface coating, lubrication, adhesion, and colloidal stability.1 The conventional theory for representing the microstructures of polymers at interface, under confinement or in the bulk, is primarily from the self-consistent-field theory,2 which takes a coarse-grained approach to describe interactions between polymeric molecules. Similar to the Flory–Huggins theory for the thermodynamic properties of bulk polymeric systems, the self-consistent-field theory usually assumes that the short-ranged repulsion between segments can be represented by the single occupancy of a lattice site or the condition of incompressibility and the intersegment attraction can be described by a van der Waals-type mean-field approximation. Despite its simplicity in terms of the segment-level description of polymeric molecules, the self-consistent-field theory has been remarkably successful to capture the qualitative and very often quantitative behavior of polymers at surface or under confinement.3 In particular, it provides an accurate description of the mesoscopic phase transitions of copolymers in bulk as well as under confinement.4

Whereas the usefulness of the self-consistent-field theory for polymeric systems is now well documented, alternative approaches have also been emerging in the literature aiming at bridging the microscopic structures of macromolecules and the phase behavior of materials by taking into account the segment-level interactions specifically.5–7 In addition to a number of powerful molecular simulation techniques that are able to account for the atomistic details,8 polymer integral-equation theories (IET)5 and density-functional theory (DFT) are most commonly used in the literature as alternatives to the self-consistent-field theory.6,9,10 Both approaches have a deep root in earlier developments of statistical mechanics for simple fluids.11 Different from the self-consistent-field theory, these alternative theories start with a semiempirical force field to describe the bonded and nonbonded interactions between the polymeric segments. As a result, the numerical performance of these theories can be directly tested with molecular simulations. In principle, IET is most suitable for the prediction of the structure and thermodynamic properties of polymeric systems in bulk while DFT is more convenient for system under confinement or for studying interfacial properties. However, the disparity becomes less distinctive if one recognizes that these two approaches are often closely tied to each other.10,12

Whereas the mathematic framework of DFT is exact, its performance for a specific system entirely depends on how the grand potential functional is formulated. In our previous work, we have developed a new version of density-functional theory of polymeric fluids where the grand potential functional is formulated. In our previous work, we have developed a new version of density-functional theory of polymeric fluids where the grand potential functional consists of an ideal part that is exact and an excess part arising from nonbonded intersegment interactions as well as the correlations of segment densities due to the chain connectivity.5,7,11 The ideal part of the grand potential takes into account the arbitrary chemical topology of individual molecules and all bonded interactions including those related to bond length, bond angle, and dihedral angles. For the excess part, we follow an earlier idea proposed by Woodward14 with the conjecture that it can be fully determined by the segment-level density profiles. The excess part of the grand potential includes contributions due to the short-
ranged and long-ranged intersegment interactions as appeared in the DFT of atomic fluids. Toward that end, a modified fundamental measure theory\textsuperscript{15,16} is employed to represent the Helmholtz energy functional due to the short-ranged repulsions while the long-ranged van der Waals attractions are accounted for using a quadratic density expansion of the excess Helmholtz energy functional.\textsuperscript{17} The effect of chain connectivity on the correlation of segment-density distributions is taken into account by extending thermodynamic perturbation theory to inhomogeneous systems.\textsuperscript{6,18} We have demonstrated that in comparison with the simulation results, this new version of density-functional theory is numerically efficient and more accurate than alternative approaches in the literature, in particular, for systems at high packing densities.

In this article, we report an extension of our previous DFT to polymeric systems consisting of freely joined Lennard-Jones (LJ) chains as often employed in molecular simulations. An extension of the hard-sphere-chain model as considered in our previous work to soft-sphere chains requires first a modification of the Helmholtz energy functional due to the short-ranged repulsion and more importantly, a cavity correlation function (CCF) that is used as an input for the thermodynamic perturbation theory. For that purpose, we follow the conventional liquid-state theories to represent the short-ranged repulsion in terms of an effective hard-sphere potential with an effective diameter,\textsuperscript{22}

\begin{equation}
   d = \frac{1 + 0.2977T^*}{1 + 0.331 63T^* + 0.001 047 71T^{*2}} \sigma,
\end{equation}

where \( T^* = \frac{k_B T}{\epsilon} \) with \( k_B \) being the Boltzmann constant and \( T \) being the absolute temperature. For a direct comparison with the simulation results, we also consider a truncated-and-shifted LJ potential for interactions between polymer segments,

\begin{equation}
   u(r) = \begin{cases} 
   4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right], & r \leq r_c, \\
   0, & r > r_c,
   \end{cases}
\end{equation}

where \( \sigma \) and \( \epsilon \) are the size and energy parameters of the LJ potential, respectively. For the full LJ potential, the cutoff distance is infinity. As originally introduced in the Baker-Henderson perturbation theory,\textsuperscript{21} the LJ potential can be further divided into a short-ranged repulsion and a long-ranged attraction,

\begin{equation}
   u^{\text{rep}}(r) = \begin{cases} 
   4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right], & r \leq \sigma, \\
   0, & r > \sigma,
   \end{cases}
\end{equation}

\begin{equation}
   u^{\text{att}}(r) = \begin{cases} 
   0, & r \leq \sigma, \\
   4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right], & \sigma < r \leq r_c.
   \end{cases}
\end{equation}

The repulsive part of the LJ potential can be approximated by a hard-sphere (HS) potential with an effective diameter,\textsuperscript{22}

\begin{equation}
   u(r) = -\frac{4\epsilon}{\left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6}},
\end{equation}

According to Eq. (5), the pair potential becomes continuous at the cutoff distance. To relate the truncated-and-shifted LJ potential to the truncated potential, we define a residual interaction potential,

\begin{equation}
   u^{\text{res}}(r) = \begin{cases} 
   -4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right], & r \leq r_c, \\
   0, & r > r_c.
   \end{cases}
\end{equation}

Therefore, the truncated-and-shifted LJ potential can be expressed in terms of Eq. (1) plus a residual potential Eq. (6). For a freely jointed LJ chain, the bonding potential is described by

\begin{equation}
   \exp[-\beta V_b(R)] = \prod_{i=1}^{M-1} \frac{\delta(|r_{i+1} - r_i| - \sigma)}{4\pi \sigma^2},
\end{equation}

where \( M \) stands for the number of segments for each chain, \( R = (r_1, r_2, \ldots, r_M) \) denotes a set of coordinates describing the segmental positions, \( \delta \) is the Dirac-delta function, and \( \beta = 1/k_B T \).
The grand potential functional \( \Omega[\rho_M(R)] \) of a one-component polymeric fluid is related to the Helmholtz energy functional \( F[\rho_M(R)] \) by the Legend transformation,

\[
\Omega[\rho_M(R)] = F[\rho_M(R)] + \int [V_M(R) - \mu_M] \rho_M(R) dR, \tag{8}
\]

where \( dR = dr_1 dr_2 \ldots dr_M \) represents a set of differential volumes, \( \rho_M(R) \) is the chain density as a function of segment positions \( R \), \( \mu_M \) is the chemical potential of a chain molecule, and \( V_M(R) \) denotes the external potential applying to each molecule. The total external potential is equal to the summation of the external potential energy on individual segments, i.e., \( V_M(R) = \sum_{i=1}^{M} V_i(r, \sigma) \). For homopolymer chains, the overall number density of segments \( \rho(r) \) is defined as

\[
\rho(r) = \sum_{i=1}^{M} \rho_i(r) = \sum_{i=1}^{M} \int dR \delta(r - r_i) \rho_M(R). \tag{9}
\]

The central task of DFT is to derive an analytical expression for the Helmholtz free energy as the functional of the density profile \( \rho_M(R) \).

Without loss of generality, the intrinsic Helmholtz energy functional \( F \) can be further decomposed into that for the ideal chains where all nonbonded intermolecular interactions are turned off and excess terms due to intersegmental interactions and chain connectivity, i.e.,

\[
F[\rho_M(R)] = F^{\text{id}}[\rho_M(R)] + F^{\text{ex}}[\rho_M(R)] - F^{\text{res}}[\rho_M(R)]. \tag{10}
\]

where is the corresponding intrinsic Helmholtz free energy for an ideal gas of polymeric molecules, \( F^{\text{id}}[\rho_M(R)] \) represents the contribution to the excess Helmholtz free energy due to the hard-sphere (HS) of repulsions, \( F^{\text{ex}}[\rho_M(R)] \) is that due to the effect of chain connectivity on intersegment correlation, \( F^{\text{res}}[\rho_M(R)] \) is the contribution due to attraction, and \( F^{\text{res}}[\rho_M(R)] \) represents a residual term caused by the potential shift. According to Eq. (10), the excess Helmholtz energy functional depends solely on the segmental density profiles.

The ideal-gas term is known exactly. It depends on the molecular configurations and the details of the bonding potential \( V_M(R) \),

\[
\beta F^{\text{id}} = \int dR \rho_M(R) \ln \rho_M(R) - 1
\]

\[
+ \beta \int dR \rho_M(R) V_M(R). \tag{11}
\]

In Eq. (11), the cube of the thermal wavelength \( \Lambda^3 \) is omitted from \( \ln \rho_M(R) \) because it makes no direct contribution to the density profiles or thermodynamic properties.

As in our previous work, the excess Helmholtz free energy due to the HS repulsion \( F^{\text{ex}}_{ss} \) is represented by a modified fundamental measure theory (MFMT),

\[
\beta F^{\text{ex}}_{ss} = \int \Phi_{bs} \delta[n_s(r)] dr, \tag{12}
\]

in which the reduced excess energy density \( \Phi_{bs} \) is expressed as a function of six weighted densities \( n_s(r) = \int \rho(r') \omega^{(s)}_l |r - r'| dr' \). Without loss of generality, the intrinsic Helmholtz expression is correlated in the density and temperature ranges of 0.005 \( \leq \rho^* \leq 1.25 \) and 0.7 \( \leq T \leq 6.0 \), we find that it remains highly accurate for 0.6 \( \leq T \leq 10.0 \) when \( \rho^* \leq 1.25 \).

The detailed expression for \( n_s \) can be found in our previous publications. For the LJ potential, the effective hard-sphere diameter \( d \) instead of the LJ diameter \( \sigma \) should be used to calculate the weighted densities. We assume that the excess Helmholtz free energy for chain connectivity \( F^{\text{ex}}_{ch} \) can also be expressed in terms of the weighted densities,

\[
\beta F^{\text{ex}}_{ch} = \int dr \Phi_{ch} \delta[n_s(r)]. \tag{14}
\]

For a bulk fluid, the first-order thermodynamic perturbation theory gives

\[
\Phi_{bs} = \frac{1 - M}{M} \rho_b \ln y_b, \tag{15}
\]

where \( \rho_b \) and \( y_b \) are the segment density and the CCF, respectively. According to previous Monte Carlo simulations for the equation of state of LJ chains, the CCF can be empirically correlated in terms of the average density and reduced temperature,

\[
y_b = 1 + \sum_{i,j=1}^{5} a_{ij}(\rho^*)(T^*)^{i-j}, \tag{16}
\]

where \( a_{ij} \) represents 25 density-independent empirical constants and \( \rho^* = \rho \sigma^3 \) denotes the reduced density. Although this expression is correlated in the density and temperature ranges of 0.005 \( \leq \rho^* \leq 1.25 \) and 0.7 \( \leq T \leq 6.0 \), we find that it remains highly accurate for 0.6 \( \leq T \leq 10.0 \) when \( \rho^* \leq 1.25 \). Equation (16) is extended to inhomogeneous systems by replacing \( \rho^* \) and \( \rho_b \) by \( n_s(6\sigma^3/\pi d^3) \) and \( n_s \xi \), respectively,

\[
\Phi_{ch} = \frac{1 - M}{M} n_s \xi \ln y(n_s), \tag{17}
\]

\[
y(n_s) = 1 + \sum_{i,j=1}^{5} a_{ij}(n_s)(6\sigma^3/\pi d^3)(T^*)^{i-j}, \tag{18}
\]

where \( \xi = 1 - n_{ss} n_{s2} n_{s3}^2 \) stands for the inhomogeneity factor. A similar approach has been used in our previous work for the DFT of hard-sphere chains. Unlike an equation of state for bulk polymeric fluids, we find that the performance of DFT degrades appreciably if the CCF in Eq. (17) is replaced by that for HS chains.
Following our previous work for monomeric LJ fluids, the excess Helmholtz free energy due to the van der Waals attraction $F_{\text{ex}}^{\text{att}}$ is represented by a quadratic expansion with respect to the bulk density $\rho_b$ (DFT-DCF),

$$\beta F_{\text{ex}}^{\text{att}} = \beta F_{\text{ex}}^{\text{att}}(\rho_b) + \int_\mathbb{R} d\mathbf{r} \beta \mu^{\text{att}}[\rho(\mathbf{r}) - \rho_b]$$

$$- \frac{1}{2} \int_\mathbb{R} d\mathbf{r} d\mathbf{r}^\prime C^{\text{att}}(|\mathbf{r} - \mathbf{r}^\prime|)[\rho(\mathbf{r}) - \rho_b][\rho(\mathbf{r}^\prime) - \rho_b],$$

(19)

where $F_{\text{ex}}^{\text{att}}(\rho_b)$ and $\mu^{\text{att}}$ represent the Helmholtz energy and the chemical potential due to the attractive potential in the bulk limit, respectively. Upon the functional derivative of the Helmholtz energy with respect to the density profiles, the first item on the right-hand side of Eq. (19) vanishes and the second item cancels with that appeared in the bulk chemical potential. The analytical expression of the DCF due to the long-ranged attraction $C^{\text{att}}(r)$ is derived from the first-order MSA. The expression for the DCF is reproduced in the Appendix with some minor changes for the systems considered in this work.

Alternatively, the attractive part of the excess Helmholtz free energy can be represented by the mean-field approximation (DFT-MFT),

$$\beta F_{\text{ex}}^{\text{att}} = \frac{1}{2} \int_\mathbb{R} d\mathbf{r} d\mathbf{r}^\prime \beta \mu^{\text{att}}(|\mathbf{r} - \mathbf{r}^\prime|) \rho(\mathbf{r}) \rho(\mathbf{r}^\prime).$$

(20)

In our previous work, we have demonstrated that Eq. (20) is not very reliable for monomeric LJ fluids despite its broad application in the literature. To facilitate a direct comparison between Eqs. (19) and (20), the performance of the mean-field theory for LJ chains is also investigated in this work.

Finally, the Helmholtz free energy due to the residual potential is accounted for by using the mean-field approximation,

$$\beta F_{\text{ex}}^{\text{res}} = \frac{1}{2} \int_\mathbb{R} d\mathbf{r} d\mathbf{r}^\prime \beta \mu^{\text{res}}(|\mathbf{r} - \mathbf{r}^\prime|) \rho(\mathbf{r}) \rho(\mathbf{r}^\prime).$$

(21)

Because the residual potential can be made arbitrarily small in comparison with the full LJ potential, the error introduced by the mean-field approximation here is expected to be negligible.

The equilibrium density profile of LJ chains satisfies the Euler–Lagrange equation, derived from the minimization of the grand potential,

$$\rho_M(\mathbf{R}) = \exp[\beta \mu_M - \beta V_b(\mathbf{R}) - \beta \Lambda(\mathbf{R})].$$

(22)

In Eq. (22), $\Lambda(\mathbf{R}) = \delta F_{\text{ex}} / \delta \rho_M(\mathbf{R})$ represents an effective potential field due to nonbonded intra- and intermolecular interactions. Because the excess Helmholtz energy functional depends only on the segment density, the effective self-consistent molecular potential can be written as

$$\Lambda(\mathbf{R}) = \frac{\delta F_{\text{ex}}}{\delta \rho_M(\mathbf{R})} = \sum_{j=1}^M \frac{\delta F_{\text{ex}}}{\delta \rho(\mathbf{r}_j)}.$$  

(23)

Substituting Eq. (23) into Eq. (22) yields

$$\rho_M(\mathbf{R}) = \exp \left[ \beta \mu_M - \beta V_b(\mathbf{R}) - \beta \sum_{j=1}^M \lambda(\mathbf{r}_j) \right]$$

(24)

with

$$\lambda(\mathbf{r}_j) = \frac{\delta F_{\text{ex}}}{\delta \rho(\mathbf{r}_j)} + v(\mathbf{r}_j).$$

(25)

From Eqs. (9) and (24), we can calculate the segment density $\rho_s(\mathbf{r})$ from

$$\rho_s(\mathbf{r}) = \int d\mathbf{R} (\delta(\mathbf{r} - \mathbf{r}_i) \exp \left[ \beta \mu_M - \beta V_b(\mathbf{R}) - \beta \sum_{j=1}^M \lambda(\mathbf{r}_j) \right]$$

(26)

and the overall segment density is equal to the summation of the densities for all segments,

$$\rho(\mathbf{r}) = \int d\mathbf{R} \sum_{i=1}^M (\delta(\mathbf{r} - \mathbf{r}_i) \exp \left[ \beta \mu_M - \beta V_b(\mathbf{R}) - \beta \sum_{j=1}^M \lambda(\mathbf{r}_j) \right]$$

(27)

Equations (26) and (27) are used to solve the density profiles following a Picard iteration method as discussed earlier.

III. CONFIGURATIONAL-BIAS MONTE CARLO SIMULATIONS

To test the numerical performance of the DFT, we have also carried out $NVT$ configurational-bias Monte Carlo simulations for freely jointed LJ polymers confined in attractive or hard slit pores. For a given pore width and an average polymer packing fraction $\eta_{av}$, the simulation box contains at least 50 polymer chains. The period boundary conditions are applied to the $x$ and $y$ directions of the simulation box; the box length in the $z$ direction is fixed by the pore width. The recoil-growth algorithm is used to generate the initial polymer configurations, followed by translational, rotational, and configurational-biased (including chain regrowing, and cut-rebridging) Monte Carlo moves. The different methods for Monte Carlo updates are allocated approximately with equal frequency. Each simulation runs $1 \times 10^7$ Monte Carlo cycles, with the first half for the system to reach equilibrium whereas the second half for evaluating the ensemble averages.

IV. RESULTS AND DISCUSSION

In this section, we show some illustrative examples on the performance of the polymer DFT for freely jointed LJ chains by a direct comparison with the results from molecular simulations. Three different situations are considered: the structures of LJ chains in slit pores, around isolated nanoparticles, and in bulk. For the bulk case, the inter- and intramolecular correlation functions are calculated following an extended test-particle method introduced in our earlier work.
A. Inside a slit pore

For freely joined tangent LJ chains confined in an attractive slit pore, the interaction between each segment and a slit surface is given by the Steele’s 10-4-3 potential,

\[
V(z) = \epsilon_0 \left( \frac{2}{5} \frac{\sigma_w}{z} \right)^{10} - \left( \frac{\sigma_w}{z} \right)^{4} - \frac{\sigma_w^4}{3\Delta(z + 0.61\Delta)^3},
\]

in which the parameters are related to those of the LJ potential by

\[
\sigma_w = \sigma, \ \epsilon_w = 6.283\epsilon, \ \Delta = 0.7071\sigma.
\]

Equation (28) is widely used in the literature for modeling the interaction between a fluid molecule and a planar layered surface such as carbonaceous materials. In a symmetric slit pore, the external potential for each segment is given by

\[
v(z) = V_s(z) + V_s(H-z),
\]

with \(H\) being the pore width and \(z\) being the perpendicular distance from the surface. For chains confined in hard slit pores, the external potential is given by

\[
v(z) = \begin{cases} 
\infty & \text{if } z < 0.5\sigma \text{ or } z > H - 0.5\sigma \\
0 & \text{otherwise}
\end{cases}
\]

Relatively short chains of \(M=4, 8,\) and 16 are used for the comparison between the DFT and Monte Carlo calculations considering that the Monte Carlo simulation of longer chains is rather time consuming. In both DFT and MC calculations, the cutoff distance for the intersegment LJ potential is set to \(r_c = 2.5\sigma.\) The calculation is carried out at fixed pore width \(H^* = H/\sigma = 8.0.\) The average packing fraction in the pore is defined as

\[
\eta_{av} = \frac{\pi}{6\bar{H}} \int_0^H \rho^*(z)dz.
\]

Figure 1 depicts the reduced segment densities of LJ chains within an attractive slit pore calculated from the DFT. Also shown in this figure are the corresponding results from NVT simulations. Here the average packing fraction is fixed at \(\eta_{av} = 0.1\) and two temperatures \(T^* = 1.0\) and 4.0 are considered, corresponding to conditions below and above capillarity condensation inside the pore, respectively. Because of the symmetry of the slit pore, we present only the left half of the density profiles. Interestingly, Fig. 1 shows that the performance of the DFT using Eq. (19) or (20) is nearly indistinguishable and both methods perfectly reproduce the simulation results. The good performance of the mean-field theory is mainly because the average polymer packing densities are fixed so that the errors introduced in the bulk equation of state and mean-field density cancel each other. At low temperature, the polymer molecules are accumulated near the surface forming a layer-by-layer structure similar to that for a monomeric LJ fluid. The layering structure is related to the strong attractions from the surface and from the adsorbed molecules. At high temperature, however, the entropy penalty for the confinement of the polymer chains becomes more significant, as shown in the dampened peaks of the density profiles. In this case, the density profiles decay slowly and the inhomogeneity vanishes far from the surface.

![Figure 1. Segment-density profiles of LJ chains in an attractive slit pore with the reduced pore width \(H^*=8.0.\) For all the cases, the average packing fraction in the bulk is \(\eta_{av}=0.1\) and the reduced temperature is (a) \(T^*=1.0\) and (b) \(T^*=4.0.\) The symbols represent the simulation results for \(M=4\) (cycles), \(8\) (squares), and \(16\) (triangles), and the solid and dashed lines are the results of DFT-DCF and DFT-MFT, respectively. For clarity, profiles for \(M=8\) and 16 have been consecutively shifted upward by one unit for \(T^*=1.0\) and by 0.2 units for \(T^*=4.0.\)

B. Around an isolated nanoparticle

We now apply the DFT to particle/ LJ chain mixtures by calculating the morphology of the polymeric molecules around an isolated nanoparticle. Such system represents a “primitive” model for the infinite dilution of colloidal particles in a polymer solution. Following a recent simulation from the literature,\(^2\) we assume that the colloid-segment interaction is represented by the full-ranged LJ potential,

\[
u_{cs}(r) = 4\epsilon_{cs} \left[ \frac{\sigma_c + \sigma}{2r} \right]^{12} - \left( \frac{\sigma_c + \sigma}{2r} \right)^{6},
\]

where \(\sigma_c\) is the colloidal diameter, \(\epsilon_{cs}\) is the colloid-segment energy parameter. The intersegment LJ potential is cut and shifted with the cutoff distance set to \(r_c = 2.5\sigma.\) The reduced segment density of LJ chains in the bulk \(\rho^*\) and the reduced
temperature $T^*$ are fixed at 0.05 and 3.0, respectively. For a direct comparison with the simulation results, we investigate the dependence of the segment-density distribution around the colloidal particle on the particle diameter $s_c$, the number of segments per chain ($d M$), and the reduced colloid-segment temperature $T_{cs}^* = k_B T / \varepsilon_{cs}$.

Figure 3 shows the effect of the particle diameter on the colloid-segment pair distribution $g_{cs}(r)$ at different chain lengths $M=20$, and $T_{cs}^* = 3.0$. The enhancement of the local polymer segment density (adsorption) near the colloidal surface is magnified as the particle diameter increases. This is primarily due to the increase of the range of the LJ attraction between the particle and the polymer segments because at fixed surface energy, we would expect a decline of surface adsorption as the particle size increases. The discrepancy between the DFT and simulation is partially due to the approximate nature of the theory but more likely due to the accuracy of simulations because the bulk value of the density is not recovered far from the particle surface. With the total number of polymer chains fixed, an increase in the simulation density far from the particle surface will lead to a reduction of the density peak thus improve the agreement with the DFT.

Figure 4 compares the colloid-polymer distribution $g_{cp}(r)$ at different chain lengths but fixed colloidal diameter $s_c = 10$, and $T_{cs}^* = 3.0$. Interestingly, the polymer segment density near the colloid surface increases with the polymer chain length. As shown late in Fig. 5, the accumulation of segments near the particle is due to surface adsorptions. Figure 5 depicts the effect of the colloid-segment interaction energy on the segment-density profile at $s_c = 10 \sigma$ and $M = 20$. At high values of $T_{cs}^*$ or low surface energy, there is a depletion of polymer segments near the colloidal particle. The depletion layer diminishes when $T_{cs}^*$ is reduced or equivalently the surface energy is increased. For $T_{cs}^* > 6.0$, a strong increase in $g_{cp}(r)$ is observed near the particle surface. The agreement between the density profiles predicted from
DFT and MC is satisfactory. Both theory and simulations indicate that an increase in the particle size, polymer chain length, and the particle-segment attraction will lead to a stronger polymer adsorption at the particle surface. In general, the prediction of DFT based on the quadratic expansion is slightly better than that from the mean-field theory, in particular, near larger particle size, for longer chain length or higher surface energy. However, the discrepancy is not substantial for most cases considered in this work. Some noticeable disagreement between the DFT and simulation is observed at large values of particle size $s_c$ and chain length $M$ or surface energy $1/T_{cs}$. Because in all these cases, the simulation fails to reproduce the bulk segment density far from the particle surface, we suspect the discrepancy likely arises from the simulations rather than the approximate nature of the DFT.

C. Inter- and intramolecular correlation functions

We have shown in Secs. IV A and IV B that the DFT is quantitatively accurate for predicting the structures of confined LJ chains. To test its performance for predicting the correlation functions of bulk fluids, we calculate the intra- and intermolecular correlation functions of freely jointed LJ chains using an extended test-particle method proposed earlier. The inter- and intramolecular correlation functions are defined as

$$g_{\text{inter}}(r) = \frac{1}{M^2} \sum_{i=1}^{M} \sum_{j=1}^{M} \rho_a^{A}_{i,j} \rho_b,$$  \hspace{1cm} (34)

$$\omega(r) = \frac{1}{M} \sum_{i=1}^{M} \sum_{j=1}^{M} \rho_a^{B}_{i,j},$$  \hspace{1cm} (35)

where $\rho_a^{A}_{i,j}$ and $\rho_a^{B}_{i,j}$ are, respectively, the density profiles of a segment $i$ from the free chains and the tethered chain that is fixed at the segment $j$.

Figures 6–8 present the inter- and intramolecular correlation functions of freely jointed LJ chains predicted by the DFT along with the simulation results that are attainable from the literature.\textsuperscript{29,30} In these calculations, the intersegment interaction is represented by the full LJ potential and the reduced temperature $T^*$ is fixed at 8.0. Apparently, the DFT is able to capture the intersegment depletion at low density and the excluded-volume effect at high density; both in qualitative agreement with experiments. In particular, the DFT provides the segment-level details of the density profiles such as the cusp around $2\sigma$ and reproduces faithfully the long-ranged intersegment correlations at low density. In comparison with the simulation results, the present DFT overpredicts slightly the excluded-volume effect, in particular, at high densities. The discrepancy is likely attributed to the intersegment long-ranged correlations introduced by the chain connectivity, which is taken into account only within the first-order thermodynamic perturbation theory. Indeed, the effect of chain connectivity on intersegmental depletion is magnified with the increase of chain length, as clearly depicted in Figs. 6–8.

The discontinuity of intramolecular correlation functions at $r=2\sigma$ arises from the direct interaction between two near-
est neighbors bonded to a test segment. For $r > 2\sigma$, the DFT reproduces the monotonic decaying of the intramolecular correlation functions almost quantitatively. When the distance is less than $2\sigma$, the discrepancy between the DFT and simulation is likely due to the underestimation of the inter-segment correlations due to the chain connectivity. Again, for all the cases considered here, we find that the difference between the calculated results from Eqs. 19 and 20 is negligible, suggesting that the mean-field approximation for van der Waals attraction works reasonably well for polymeric fluids.

V. CONCLUSIONS

We have extended our recent work on the density-functional theory of polymeric fluids to Lennard-Jones (LJ) chains with explicit consideration of segment size, van der Waals attraction, and structural correlations due to chain connectivity. By an extensive comparison with the simulation results from the literature and from this work, we find that the short-ranged soft repulsion can be successfully taken into account using an effective hard-sphere model and the van der Waals attractions can be represented by either the mean-field approximation or the density expansion of the excess Helmholtz energy functional. Apparently, the mean-field approximation for polymeric fluids performs much more reasonably than that for corresponding monomeric systems, at least for all the cases considered in this work. In general, the agreement between simulation and DFT is very good at a variety of thermodynamic conditions at both high and low densities and temperature limits. Because Monte Carlo simulation for systems containing long polymer chains is rather computationally demanding, only relative short chains are considered in this work. Nevertheless, the application of DFT is not limited to short chains.

Inter- and intramolecular correlation functions of polymeric fluids play an important role in providing useful information on chain size, polymer configurations, and aggregation and collapse of polymer chains. However, a faithful description of the segment-level structures of polymeric molecules remains a serious theoretical challenge. The conventional approach for predicting the inter- and intramolecular correlation functions of polymeric fluids is from the integral-equation theory (IET),31 in particular, the polymer reference interaction site model (PRISM). PRISM is able to provide good predictions of the intermolecular correlation functions provided that the intramolecular correlation function can be estimated independently. By applying a recently proposed extended test-particle method, we find that the DFT provides a self-contained approach in calculating the inter- and intramolecular structures of polymeric fluids.13,27 In comparison with PRISM, the main advantage of DFT approach is that it is self-contained, i.e., it employs no a priori assumptions or simulation input.

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APPENDIX: DIRECT CORRELATION FUNCTION FROM THE MEAN-SPHERICAL APPROXIMATION (MSA)

According to the first-order MSA theory, the direct correlation function due to the LJ attraction is given by17

$$C^{\text{att}}(r) = \begin{cases} e^{\text{Yukawa}}(T_1^r, \frac{r}{d}, \frac{r}{\sigma^2}) - e^{\text{Yukawa}}(T_2^r, \frac{r}{d}, \frac{r}{\sigma^2}), & r < d \\ 0, & d \leq r < \sigma \\ -\frac{4}{\sqrt{T}} \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right], & r \geq \sigma \end{cases}$$

with

$$k_0 = 2.1714\sigma, \quad k_1 = k_0 \exp[z_1(\sigma - d)],$$

$$k_2 = k_0 \exp[z_2(\sigma - d)],$$

FIG. 8. Same as in Fig. 6 but for $\rho^*=0.102$ and 0.5 at $M=16$. The simulation data are from Ref. 30. The curves for $\rho^*=0.5$ have been shifted upward by one unit.
In Eq. (A1), the first-order Yukawa DCF is

$$c_i^{\text{Yukawa}}(T^*, z, r) = \frac{\exp[-(r-1)]}{rT'} - \left\{ \begin{array}{l}
S^2(z)\exp[-(r-1)] + 144\eta L(z)\exp[(r-1)] \\
- 12\eta^2[(1+2\eta^2)^2 + (1-\eta)(1+2\eta)^2]r^4 \\
+ 12\eta S(z)L(z) - (1-\eta)(1+0.5\eta)z^6 \eta^2r^2 \\
- 24\eta[(1+2\eta)^2z^4 + (1+2\eta^2)z^6r] \\
+ 24\eta S(z)L(z)
\end{array} \right\} \frac{1}{r(1-\eta)^4z^8Q^2(z)T'}$$

with

$$Q(x) = \frac{S(x) + 12\eta L(x)\exp(-x)}{(1-\eta)^2x^3},$$

$$S(x) = (1-\eta)x^3 + 6\eta(1-\eta)x^2 + 18\eta^2x - 12\eta(1+2\eta),$$

$$L(x) = (1 + 0.5\eta)x + 1 + 2\eta,$$

$$\eta = \frac{1}{3}\pi pd^3.$$


