

**Nematic-isotropic phase transition in diblock fused-sphere chain fluids**

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A density-functional theory for the isotropic-nematic phase transition in fluids of rigid or semiflexible fused hard-sphere chains, developed previously by the authors, is extended to diblock chains each consisting of both a rigid and a flexible part. The theory is compared with recent Monte Carlo simulation results of McBride *et al.* The theoretical results for the variation of pressure and nematic order parameter with density agree well with the simulation data over density ranges where the simulations find isotropic and nematic phases.

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In recent years, the system of hard-sphere chains has been widely studied as a coarse-grained model for polyatomic molecular fluids, including polymers. Many of these theoretical studies have been based on methods such as Wertheim's thermodynamic perturbation theory (TPT) [1,2] and generalized Flory dimer theory [4,3], which are limited to describing uniform isotropic fluid phases. Several density-functional methods [5–10] have been developed to extend these treatments to nonuniform and/or liquid-crystalline systems. Increasingly, computer simulation methods [7,8] have also been used to study the structure, thermodynamics, and interfacial behavior of hard-sphere chain fluids. The majority of these studies have focused on *tangent* hard-sphere chains, where the bond length  $l$  (i.e., distance between adjacent spheres) equals the hard-sphere diameter  $d$ . Until quite recently, the only computer-simulation study of liquid-crystal formation in *fused* hard-sphere chain fluids, where  $l < d$ , was that of Whittle and Masters [11]. Subsequently, McBride *et al.* [12,13] have simulated several fused-sphere models to determine their liquid-crystalline and solid phases. A related study of a soft-repulsive-sphere chain fluid has been described by Tian *et al.* [14].

In previous work [6], we developed a density-functional theory for the nematic-isotropic phase transition in fluids of both rigid and semiflexible hard-sphere chains. While the results of the theory compared well with simulation data [7,8] for tangent hard-sphere chains, we found lesser agreement with the simulation results of Whittle and Masters [11] for fused-sphere chains, especially for the variation of pressure with density. Hence it is worthwhile to compare the theory of Ref. [6] with the more recent simulation results of McBride *et al.* [12,13]. The fused-sphere system with arbitrary  $l/d$  is more general than the tangent-sphere system studied in most previous work, as it allows for variation in the degree of convexity of the molecules [13] and more accurately models the chemical structure (in terms of bond lengths) of polyatomic molecules [2]. Aside from work of Varga and Szalai [15], which was restricted to *rigid* linear molecules, we are not aware of any other density-functional

studies of liquid-crystal formation in systems of fused hard-sphere chains. Here, following McBride *et al.* [12,13], we also examine fluids of *diblock* fused-sphere chains, where each molecule consists of both a rigid and a flexible part, which more realistically model typical mesogenic molecules.

The theory [6], currently restricted to spatially uniform systems, accounts for nonideal contributions to the Helmholtz free energy, resulting from intermolecular repulsive interactions, by means of scaled-particle theory [16,17]. We refer the reader to Ref. [6] for most of the details, but will point out that a fundamental quantity involved is the excluded volume between two molecules. For rigid linear molecules consisting of fused hard spheres, this is given analytically [18] by the generalization of a result first derived for tangent-sphere chains by Williamson and Jackson [19]. It was shown in Ref. [6] that the orientation-dependent excluded volume for rigid chains could be expressed as the mean excluded volume of an appropriate "binary mixture" of hard-sphere monomers and dimers. For semiflexible chains, the key approximation made in Ref. [6] is that the excluded volume between two chains can be analogously expressed in terms of monomer and dimer contributions. This feature is similar to that occurring in the self-consistent field theory of Khokhlov and Semenov [20,21] for wormlike chains, which decomposes a polymer into linear submolecules of cylindrical shape. Calculations based on the theory involve solving a nonlinear self-consistency equation for the chain-averaged distribution function of dimer orientations (which is equivalent to the orientation distribution function of the whole molecule when the latter is rigid). In the case of semiflexible chains, the solution of the self-consistency equation entails additional statistical averaging over all single-chain conformations. In practice, this averaging is done by partial enumeration over a large number ( $10^6$ – $10^7$ ) of self-avoiding chain conformations, similar to other work [10]. The particular diblock models simulated in Refs. [12,13] consist of chains containing a total of  $n=15$  hard-sphere monomers, all with the same diameter  $d$  and interatomic spacing  $l$ , of which a variable number  $n_r$  at one end of the chain are fixed in a

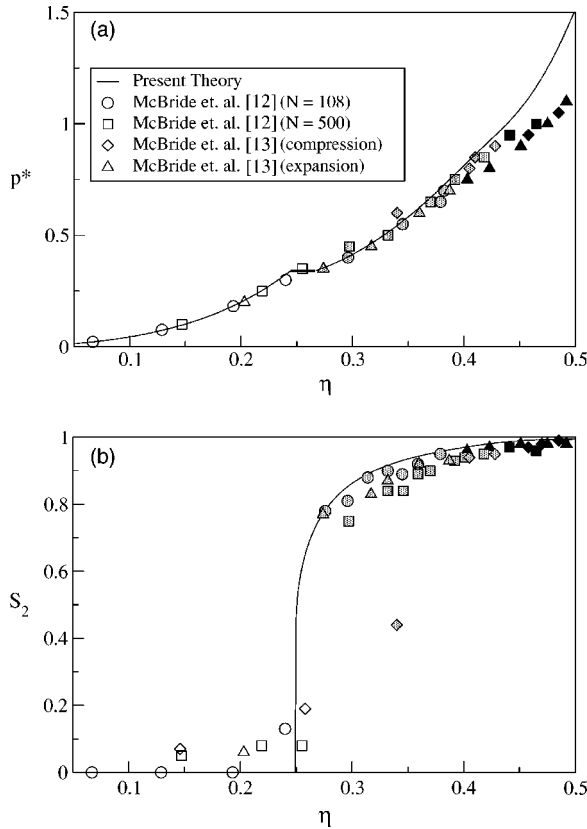


FIG. 1. Reduced pressure (a) and nematic order parameter (b) vs volume fraction for rigid 15-sphere chains. Simulation data from Refs. [12,13] are shown by white, gray-filled, and black-filled symbols, representing isotropic, nematic, and smectic phases, respectively [22].

rigid linear configuration while the remaining  $n_f = n - n_r$  monomers form a flexible tail. To apply the theory to these cases, the only modification required in the calculations is in accounting for the chain structure during the enumeration stage, which is done simply by constraining the first  $n_r$  monomers in the chain to lie in the same (random) orientation. Finally we remark that, due to its restriction to uniform systems, the theory in its present form is unable to account for smectic or crystalline phases.

The first cases examined here are completely rigid molecules consisting of 11 and 15 hard-sphere monomers fused in a linear configuration with a reduced bond length  $l^* \equiv l/d = 0.6$ . Figures 1(a) and 1(b) show the variation of the reduced pressure  $p^* \equiv pd^3/(k_B T)$  and nematic order parameter  $S_2$  with volume fraction  $\eta \equiv \rho v$ , respectively, for the 15-monomer chains. Here  $p$  is the pressure,  $\rho$  is the chain number density,  $v$  is the volume of a chain molecule, and  $S_2 = \langle P_2(\cos \theta) \rangle$ , where  $P_2$  is the second Legendre polynomial and  $\theta$  is the angle between the molecular axis and the nematic director. The solid curves show the results of the present theory, while the various symbols are the results of several different simulation runs performed in Refs. [12,13], which are explained in the legends and captions to the figures (see also Ref. [22]). The isotropic, nematic, and smectic phases identified in the simulations are distinguished by white, gray-filled, and black-filled symbols, respectively.

TABLE I. Results of present theory for the nematic-isotropic coexistence properties:  $n_r$  and  $n_f$  refer to the number of monomers in the rigid and flexible parts of the chains, respectively.

$n_r, n_f$	$\eta$ (iso)	$\eta$ (nem)	$S_2$	$p^*$
11,0	0.306	0.327	0.712	0.739
15,0	0.245	0.266	0.724	0.341
13,2	0.286	0.301	0.672	0.536
11,4	0.342	0.353	0.634	0.963
10,5	0.374	0.383	0.608	1.328
9,6	0.409	0.417	0.592	1.872
8,7	0.446	0.453	0.581	2.672

Overall, we see close agreement between theory and simulation for the behavior of the isotropic and nematic phases. Note that there is considerable uncertainty in the simulated values of  $S_2$ , highlighted by the nonzero values of this quantity in the isotropic phase. The agreement between theory and simulation for the pressure in the nematic phase is apparently much better than we found in Ref. [6], comparing the theory with earlier simulations of Whittle and Masters [11] for eight-sphere chains with  $l^* = 0.6$ . In that comparison, the theoretical values of  $p^*$  deviated increasingly from the simulation results with increasing  $\eta$ , in a manner similar to that seen here in Fig. 1(a) where the simulations indicate the presence of a smectic-A phase. There was some indication that the simulated liquid-crystalline phase in Ref. [11] may have been smectic, which could account for the discrepancy between the theory and simulation results in that case. Comparisons between the present theory and simulations of the 11-monomer chains studied in Ref. [12] are of similar quality to those in Figs. 1(a) and 1(b) and are omitted here.

The theoretical values of  $S_2$ ,  $p^*$ , and coexisting values of  $\eta$  at the isotropic-nematic transition for all models studied in this paper are listed in Table I. The precise locations of the phase transition were not determined in the simulations [12,13], due to the absence of free-energy calculations, but the graphs suggest that there is fairly close agreement with the present theoretical results.

Next we examine the diblock models studied in Refs. [12,13], where  $(n_r, n_f)$  take the values (13,2), (11,4), (10,5), (9,6), and (8,7). In those models, there are no bond bending or torsional potentials between the monomers on the flexible tails, so the latter may adopt any conformation which is free of intramolecular and intermolecular overlap. As mentioned in Ref. [12], the reduced bond length  $l^* = 0.6$  does impose a maximum bond angle between a flexible bond and the previous bond of  $67.11^\circ$ . The order parameter  $S_2$  for these models is defined as earlier, where  $\theta$  is now the angle between the nematic director and a suitable "molecular axis." As in Ref. [12], we take the latter to be the eigenvector corresponding to the smallest eigenvalue of the molecular inertial tensor.

Table I indicates that the values of the coexisting densities at the transition increase, while the differences between these densities as well as the values of  $S_2$  at the transition decrease with increasing length of the flexible tail. The detailed com-

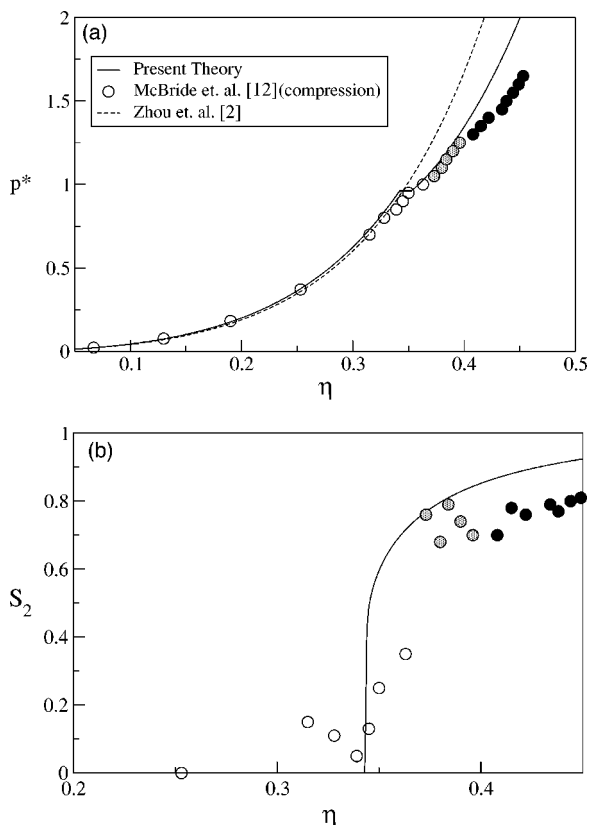


FIG. 2. Reduced pressure (a) and nematic order parameter (b) vs volume fraction for (11,4) diblock chains.

comparisons between theory and simulation results for  $S_2$  and  $p^*$  in the (13,2) case are similar to those in Figs. 1(a) and 1(b) and are omitted here. McBride *et al.* [12] concluded that the (8,7) case does not exhibit any liquid-crystalline phases for volume fractions as large as 0.48, where the behavior is found to be glassy, whereas the theory (see Table I) predicts an isotropic-nematic transition at  $\eta \approx 0.45$ .

In the remainder we focus on the two intermediate cases (11,4) and (10,5). The variations of  $p^*$  and  $S_2$  with volume fraction for the (11,4) case are shown in Figs. 2(a) and 2(b), respectively. In Fig. 2(a) we also include, as in Refs. [12,13], comparison with the pressure given by the modified TPT1 theory of Zhou *et al.* [2]. This theory only applies to the isotropic phase and, like the present theory [6], yields results in that phase which do not depend on molecular flexibility and hence for a given  $n=n_r+n_f$  are independent of the relative values of  $n_r$  and  $n_f$ . Both theories agree well with each other and with the simulation data in the isotropic phase for  $p^*$ , while the present theory predicts  $p^*$  in the nematic phase to be also in good agreement with simulation. The theoretical values of the pressure deviate from the simulation values where the latter indicate a smectic phase, similar to that seen earlier in Fig. 1(a). Both Figs. 2(a) and 2(b) suggest that the theory slightly underestimates the isotropic-nematic transition density. Note again that there is considerable spread, as well as significant “noise” (in the isotropic phase), in the  $S_2$  values determined by simulation.

Comparisons of theory and simulation results for the (10,5) case are shown in Figs. 3(a) and 3(b). The present

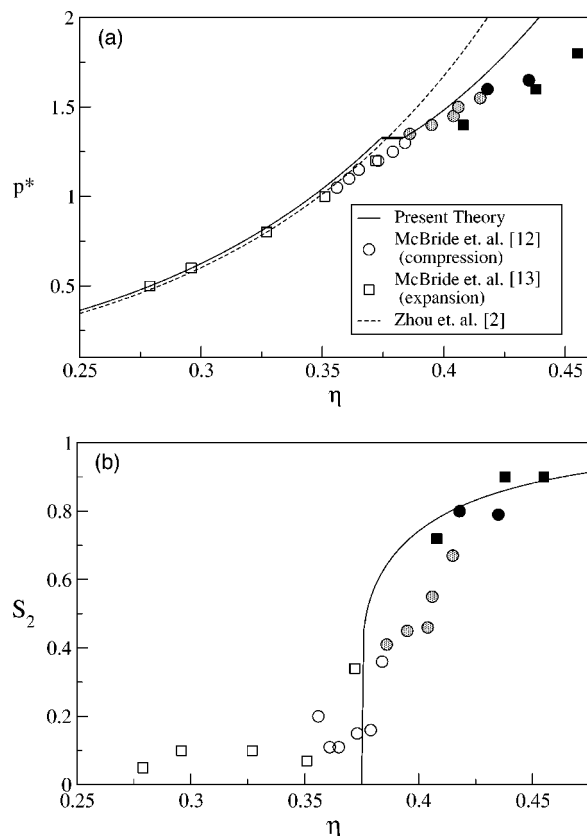


FIG. 3. Reduced pressure (a) and nematic order parameter (b) vs volume fraction for (10,5) diblock chains.

theory predicts that the nematic phase becomes stable at volume fraction  $\eta=0.383$  (see Table I). This finding and our results for the variation of pressure in Fig. 3(a) are in good agreement with the original compression runs of McBride *et al.* [12], which indicated that the nematic phase is stable between  $\eta=0.386$  and 0.415 while the smectic-A phase occurs at larger values of  $\eta$ . The simulated values of  $S_2$  in the nematic phase are seen in Fig. 3(b) to be low compared both to the theory and to simulation results for the more rigid molecules discussed earlier. The later simulations of Ref. [13] instead found, on compression, a transition from the isotropic to a metastable glassy state, although the authors suggested that these simulations were probably too short to see spontaneous formation of liquid-crystalline phases. On expansion from an initial close-packed solid structure, the simulations of Ref. [13] found a smectic-A phase between  $\eta=0.408$  and 0.499, with no indication of a nematic phase. However, there is still a “gap” in the simulated pressure and density values between the isotropic and smectic phases, see Fig. 3(a), so the existence of a nematic phase over a small range of pressures is not ruled out.

The simulation studies of Ref. [12] concluded that the (9,6) system does not exhibit a nematic phase and instead undergoes a direct isotropic-smectic transition. At present, our theory cannot rule this out.

In summary, the values of the pressure and order parameter predicted by the present theory are in good agreement with simulation results over density ranges where isotropic

and nematic phases are found by the simulations. While the simulations can give only approximate estimates of the coexisting densities at the isotropic-nematic transition, the theoretical results are in reasonable agreement with those estimates, although the agreement deteriorates with increasing relative size of the flexible tail. One explanation for the theory underestimating the transition densities of flexible chains is the fact that the approximation for the excluded volume, in terms of monomer and dimer contributions, overestimates the excluded volume because it neglects simulta-

neous contacts between a pair of molecules at two or more points along the chains [6]. Nonetheless, at present there is no other comparable theory available for describing semiflexible fused-sphere chain fluids. Future efforts will focus on improving the treatment of the excluded volume between semiflexible chains and extending the theory to spatially modulated phases such as smectic A.

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