

The nematic-isotropic phase transition in semiflexible fused hard-sphere chain fluids

K. M. Jaffer,^{a)} S. B. Opps,^{b)} D. E. Sullivan,^{c)} and B. G. Nickel

Department of Physics and Guelph-Waterloo Physics Institute, University of Guelph, Guelph, Ontario N1G 2W1, Canada

L. Mederos

Instituto de Ciencia de Materiales, CSIC, Cantoblanco, Madrid E-028049, Spain

(Received 29 September 2000; accepted 20 November 2000)

A density-functional theory of the isotropic–nematic phase transition in both rigid and semiflexible hard-sphere chain fluids is described. The theory is based on an exact analytical evaluation of the excluded volume and second virial coefficient B_2 for rigid chain molecules, which demonstrates that B_2 in these cases is equivalent to that of a binary mixture of hard spheres and hard diatomic molecules. It is assumed that the same binary-mixture representation applies to semiflexible chains, while scaled particle theory is used to obtain the properties of the fluid at arbitrary densities. The results of the theory are in very good agreement with Monte Carlo (MC) simulation data for rigid tangent hard-sphere chains, but in lesser agreement with available MC studies of rigid fused hard-sphere chains. We find that there is reasonable agreement between the theory and MC data for semiflexible tangent chains, which improves with increasing chain length. The behavior predicted by the theory for semiflexible chains is contrasted with that given by the Khokhlov and Semenov theory of nematic ordering of wormlike polymer chains. © 2001 American Institute of Physics. [DOI: 10.1063/1.1340606]

I. INTRODUCTION

Several theories have been developed which accurately predict the thermodynamic properties of hard-sphere chain fluids, such as thermodynamic perturbation theory (TPT),^{1,2} generalized Flory dimer theory (GFD),^{3–5} scaled particle theory (SPT),^{6,7} as well as various methods combining these approaches.^{8–11} In their original forms, these theories are limited to describing only the behavior of uniform isotropic fluid phases. Recently, density-functional methods have been used to extend these theories to nonuniform^{12–14} and liquid–crystalline fluids.^{15–18} Generally, the results of the latter studies have been less accurate (in comparison with computer simulation data) than the theories of uniform isotropic fluids, indicating that our fundamental understanding of the statistical behavior of such systems is still incomplete and, therefore, that further study is warranted.

In a recent article, Jaffer, Opps, and Sullivan (JOS)¹⁹ used a density-functional approach to investigate the nematic(N)–isotropic(I) phase transition in a fluid of rigid linear fused hard-sphere (LFHS) chain molecules. The JOS theory utilized a concept similar to that of TPT and GFD theories, namely representing the chain fluid by a suitable combination of reference fluids composed of hard spheres and hard diatomic molecules. A method related to the “decoupling approximation,”²⁰ originally introduced by Parsons²⁰

and Lee²¹ for a hard-spherocylinder fluid, was used to apply the theory to nematic orientationally ordered phases. The theory yielded excellent agreement for the coexisting densities of both the I and N phases and for the nematic orientational order parameter at the transition, in comparison with Monte Carlo (MC) data, but predicted pressures substantially greater than those shown by the simulations. In this article we describe a revised approach for rigid chains which significantly improves the predictions for the variation of pressure with density while maintaining excellent agreement for the transition values of the densities and order parameter. In addition, we extend the theory to semiflexible hard-sphere chain fluids, comparing results for the I – N transition in these fluids with those of recent MC simulations.^{22,23}

The theory described in this work is based on a number of different elements. We first show that the pair excluded volume and second virial coefficient B_2 for *rigid* LFHS chains can be represented exactly by that for an appropriate binary mixture of hard spheres and hard diatomic molecules. The assumption that the same binary-mixture representation of B_2 also applies to semiflexible hard-sphere chains, while not exact, underlies the extension of our theory to the latter case. It is also assumed that the thermodynamic behavior of the fluid at arbitrary density and degree of orientational order can be approximated by that of the same hard-sphere/hard-diatom mixture generated at the second virial level. This description contrasts with that of the GFD and TPT theories^{1–5} and used by JOS,¹⁹ which is based on a superposition of the behavior of *pure* hard-sphere and hard-diatom fluids. In this work, instead of the decoupling-approximation approach,¹⁹ SPT is used to obtain the properties of the fluid

^{a)}Present address: Department of Physics, McGill University, Montreal, Quebec H3A 2T8, Canada.

^{b)}Present address: Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada.

^{c)}Electronic mail: des@physics.uoguelph.ca

at arbitrary densities. Our form of SPT combines aspects of this theory developed both by Boublik and co-workers^{6,7} and by Cotter and co-workers.^{24,25} One important difference between these alternative versions of SPT, as originally formulated, is that only Cotter’s is applicable to both nematic and isotropic phases. The relations between our approach and other recent density-functional theories of nematic ordering in hard-sphere chain fluids¹⁷ as well as the Khokhlov–Semenov theory of nematic ordering in polymer chains²⁶ will be discussed.

The rest of the article is organized as follows. The theory is described in Sec. II, along with the numerical methods used in solving the theory. The results of our calculations and comparisons with other theories and with computer simulation data is described in Sec. III. In Sec. IV we present a summary and some conclusions.

II. THEORY

A. General

In this study we consider a fluid of semiflexible chain molecules (or n -mers) consisting of n overlapping hard spheres of diameter d separated by a fixed bondlength $l \leq d$, which may exhibit bond-bending and torsional degrees of freedom. The internal conformation of a molecule is characterized by the set of Euler angles $\omega_1, \omega_2, \dots, \omega_{n-1} \equiv \{\omega\}$ corresponding to the $n-1$ successive bonds in the chain, where ω_i stands for the polar and azimuthal angles (θ_i, ϕ_i) specifying the orientation of the i th bond in an arbitrary space-fixed frame. The one-molecule potential energy depending on these angles is denoted $U(\{\omega\})$, which may include bond-bending and torsional potentials as well as intramolecular hard-sphere interactions.

Considering only uniform phases of number density ρ , the variational Helmholtz free energy functional F of the fluid is

$$\frac{\beta F}{N} = \ln(\Lambda \rho) - 1 + \int d\{\omega\} f(\{\omega\}) [\ln f(\{\omega\}) + \beta U(\{\omega\})] + \frac{\beta \Delta F}{N}, \quad (1)$$

where $f(\{\omega\})$ is the normalized conformation probability distribution function of a single chain, N is the number of molecules, $\beta = 1/(kT)$, and Λ is a thermal de Broglie volume. The functional ΔF accounts for nonideal contributions to F due to intermolecular hard-core interactions. In this article we consider an approximation for ΔF analogous to those used in several recent density-functional theories of nematic ordering in rigid and semiflexible n -mers,^{15–18} based on the decoupling approximation, which is of the generic form

$$\Delta F = \Delta F(B_2^*, \eta), \quad (2)$$

where $\eta = \rho v$ is the volume fraction, v is the molecular volume, and $B_2^* \equiv B_2/v$ is the reduced second virial coefficient of the system. The free energy according to the SPT of

Cotter²⁴ also has this form. All of the above-mentioned theories^{15–18,24} can be considered as extrapolations of the exact low-density (Onsager,²⁷ $\eta \rightarrow 0$) limit,

$$\beta \Delta F/N \rightarrow B_2^* \eta, \quad (3)$$

which retain the feature that ΔF is a linear function of B_2^* at arbitrary density, but with a nonlinear dependence on η that approximately accounts for higher-order virial effects. In the original Parsons–Lee decoupling theory,^{20,21} ΔF is proportional to the excess free energy of hard spheres at volume fraction η .

The second virial coefficient B_2 for semiflexible hard-sphere n -mers is given by

$$B_2 = \frac{1}{2} \int d\{\omega\}_1 d\{\omega\}_2 f(\{\omega\}_1) \times f(\{\omega\}_2) v_e^{(n)}(\{\omega\}_1, \{\omega\}_2), \quad (4)$$

where $v_e^{(n)}(\{\omega\}_1, \{\omega\}_2)$ is the mutual excluded volume of two chains labeled 1 and 2 with conformations $\{\omega\}_1$ and $\{\omega\}_2$, respectively. Note that B_2 is a functional of the chain probability distribution function $f(\{\omega\})$. The equilibrium form of the latter is that which functionally minimizes F . Using Eqs. (1), (2), and (4), the resulting self-consistent equation for $f(\{\omega\})$ in the case of semiflexible chains is quite complicated numerically and in fact has not been studied (to our knowledge). Further progress has been achieved by making additional approximations. The theory of Fynewever and Yethiraj¹⁷ approximates Eq. (4) by replacing the full conformation probability $f(\{\omega\})$ by a ‘‘coarse-grained’’ probability depending only on the orientation of an overall molecular axis. In Sec. II B, we will describe an alternative approximation for B_2 in the case of semiflexible molecules, suggested by its form for rigid molecules, which is closely analogous to that used in the theory of Khokhlov and Semenov²⁶ for wormlike polymer chains.

B. Second virial coefficient for n -mers

In the case of perfectly rigid linear n -mers, the internal conformation of a molecule is specified by only a single Euler angle pair $\omega = (\theta, \phi)$ characterizing the orientation of the molecular axis. The conformation probability $f(\{\omega\})$ reduces to the distribution function of molecular axis orientations, $f(\omega)$, and the expression for the second virial coefficient in Eq. (4) becomes

$$B_2 = \frac{1}{2} \int d\omega_1 d\omega_2 f(\omega_1) f(\omega_2) v_e^{(n)}(\theta_{12}), \quad (5)$$

where the excluded volume $v_e^{(n)}(\theta_{12})$ now depends only on the relative angle θ_{12} between the two molecular axes. In an isotropic phase $f(\omega) = 1/(4\pi)$ while in a nematic phase, $f(\omega)$ is peaked around orientations corresponding to the direction of nematic alignment. In Ref. 19, generalizing an earlier analysis by Williamson and Jackson²⁸ which was restricted to linear tangent hard-sphere n -mers, it was shown that $v_e^{(n)}(\theta_{12})$ can be expressed exactly as

$$v_e^{(n)}(\theta_{12}) = v_e^{(n)}(0) + (n-1)^2 v_c^{(2)}(\theta_{12}), \quad (6)$$

where $v_e^{(n)}(0)$ is the excluded volume for two parallel n -mers and $v_e^{(2)}(\theta_{12})$ is the contribution from the so-called ‘‘central region’’ of the excluded volume for two hard diatomic molecules. An analytic but somewhat lengthy expression for $v_e^{(2)}(\theta_{12})$ is given in the appendix of Ref. 19, while

$$v_e^{(n)}(0) = \frac{4\pi d^3}{3} \left[1 + (n-1) \left(\frac{3l^*}{2} - \frac{(l^*)^3}{8} \right) \right], \quad (7)$$

where $l^* = l/d$ is the reduced bondlength.

We now verify that $v_e^{(n)}(\theta_{12})$ as given by the last two equations can be expressed equivalently as the mean excluded volume of a ‘‘binary mixture’’ of hard spheres (monomers) and hard diatomic molecules (dimers). That is,

$$v_e^{(n)}(\theta_{12}) = x_1^2 v_e^{(1)} + 2x_1 x_2 v_e^{(1,2)} + x_2^2 v_e^{(2)}(\theta_{12}), \quad (8)$$

where x_1 and $x_2 = 1 - x_1$ are the ‘‘mole fractions’’ of the monomers and dimers, respectively, while $v_e^{(1)} = 4\pi d^3/3$ is the excluded volume for a pair of monomers and $v_e^{(1,2)}$ is the excluded volume between a monomer and a dimer, given by

$$v_e^{(1,2)} = \frac{4\pi d^3}{3} \left[1 + \frac{3l^*}{4} - \frac{(l^*)^3}{16} \right]. \quad (9)$$

Note that both $v_e^{(1)}$ and $v_e^{(1,2)}$ are independent of molecular orientations. Comparing Eqs. (6) and (8), with $v_e^{(2)}(\theta_{12})$ in the latter given by Eq. (6) for $n=2$, one finds

$$x_2 = n - 1, \quad x_1 = 1 - x_2 = 2 - n. \quad (10)$$

The literal interpretation of x_1 and x_2 as ‘‘mole fractions’’ is, of course, unphysical (i.e., $x_2 > 1$ and $x_1 < 0$) when $n > 2$. However, we can give an alternative geometric interpretation of these relations. Note that $x_2 \equiv (n-1)$ is the number of atom–atom bonds in a chain of n atomic sites. Consider overlapping two rigid n -mers having an arbitrary relative orientation θ_{12} , to sweep out the volume excluded by one molecule to the other. One can envision carrying out this process by successively overlapping each dimer segment of one n -mer with all dimer segments on the other n -mer. Since each chain molecule contains x_2 such segments, this process immediately generates the contribution $x_2^2 v_e^{(2)}(\theta_{12})$ in Eq. (8) to the total excluded volume. The latter term overcounts the excluded volume, but that overcounting is compensated by the monomer–monomer and monomer–dimer overlap terms in Eq. (8). It can also be shown that this argument holds at the level of the position-dependent Mayer-function representation of B_2 and not only at the level of the excluded volume (which involves spatial integration of the Mayer function). The latter fact may be relevant to considering extensions of the theory to nonuniform systems.

The decomposition of $v_e^{(n)}$ and hence of B_2 into monomer and dimer contributions is reminiscent of the ideas of the TPT and GFD theories,^{1–5,19} although the latter theories utilize a superposition of the properties of pure monomer and dimer fluids rather than a ‘‘binary mixture’’ representation. In the present case, it is also to be noted that the diameter d and bondlength l of the monomer and dimer subunits are equal to those in the original n -mer, conditions which are sometimes relaxed in GFD, TPT, and related theories^{4,11} for fused-sphere models.

The key assumption we will make in generalizing the theory to semiflexible n -mers is that the excluded volume $v_e^{(n)}(\{\omega\}_1, \{\omega\}_2)$ [see Eq. (4)] can be decomposed into monomer and dimer contributions analogous to the rigid n -mer relation Eq. (8). In this case, the contribution $x_2^2 v_e^{(2)}(\theta_{ij})$ in Eq. (8) has to be replaced by summation over all dimer–dimer pairs on the two chain molecules, since the relative angles θ_{ij} between different i, j pairs are not all identical. On evaluating Eq. (4), this yields the approximation

$$B_2 \approx \frac{1}{2} \left[x_1^2 v_e^{(1)} + 2x_1 x_2 v_e^{(1,2)} + x_2^2 \times \int d\omega_1 d\omega_2 f^{(2)}(\omega_1) f^{(2)}(\omega_2) v_e^{(2)}(\theta_{12}) \right], \quad (11)$$

where the quantities $x_1, x_2, v_e^{(1)}, v_e^{(1,2)}$, and $v_e^{(2)}(\theta)$ are the same as earlier, while $f^{(2)}(\omega)$ is the normalized distribution function of *dimer* orientations. This is related to the full n -mer conformation distribution function by

$$f^{(2)}(\omega) = \frac{1}{(n-1)} \int d\{\omega\} f(\{\omega\}) \sum_{i=1}^{n-1} \delta(\omega - \omega_i). \quad (12)$$

Note that $f^{(2)}(\omega)$ averages over all dimers in the chain. The approximation, Eq. (11), for B_2 is similar to that used in the theory of Khokhlov and Semenov²⁶ for very long semiflexible polymer chains, where the dimer subunits of the present theory are replaced by rigid spherocylinders of length equal to the ‘‘persistence length’’ of the chain. In an isotropic phase, $f^{(2)}(\omega)$ equals $1/(4\pi)$ and then Eq. (11) yields the same value of B_2 as in the isotropic phase of a rigid n -mer fluid. Hence the present theory will generate identical thermodynamics for isotropic phases of rigid and semiflexible n -mers, in good agreement with computer simulation results.^{10,11,16}

C. Scaled particle theory

Now we will discuss the form of the excess free energy ΔF [see Eq. (1)] which arises in SPT.^{6–8,10,24,25} Although originally derived for rigid convex hard-core molecules, it has been argued that the theory should also be applicable to nonconvex n -mers, both rigid^{6–8} and semiflexible.¹⁰ In view of the results derived in the previous subsection, we could consider two alternative formulations of the theory, applied either to the original pure n -mer fluid or to a binary mixture of hard monomers and hard dimers with mole fractions given by Eq. (10). It is convenient to first consider the pure n -mer representation. We will actually begin with the equation of state for the pressure P . According to the SPT of both Boublik *et al.*^{6–8,10} and Cotter *et al.*,^{24,25} P is given by

$$\beta P = \rho \left[\frac{1}{1-\eta} + \frac{3\alpha\eta}{(1-\eta)^2} + \frac{3\psi\eta^2}{(1-\eta)^3} - \frac{\psi\eta^3}{(1-\eta)^3} \right], \quad (13)$$

where the parameters α and ψ are discussed below. Following Boublik *et al.*, the last term on the right-hand side of Eq. (13) is a ‘‘Carnahan-Starling’’²⁹ correction which is not included in Cotter’s work. The so-called nonsphericity parameter α is related to the reduced second virial coefficient B_2^* by

$$B_2^* = 1 + 3\alpha, \tag{14}$$

which can be verified by expanding Eq. (13) to quadratic order in ρ . For isotropic fluid phases of hard convex molecules, the relation, Eq. (14), for α in terms of B_2 agrees with that given by SPT^{6–8,10} in terms of the geometric quantities v, s , and r , where s and r are the molecular surface area and mean radius of curvature, respectively:

$$\alpha = \frac{rs}{3v}. \tag{15}$$

To apply Eq. (15) to nonconvex n -mers, for which r is ill-defined, Boublik and Nezbeda⁶ proposed approximating r by that of the corresponding spherocylindrical convex envelope. In this case, v, s , and r are given by³⁰

$$\begin{aligned} v &= v_n \equiv \frac{\pi d^3}{6} \left[1 + \frac{1}{2}(n-1)(3l^* - (l^*)^3) \right], \\ s &= s_n \equiv \pi d^2 [1 + (n-1)l^*], \\ r &= r_n \equiv \frac{d}{2} \left[1 + (n-1) \frac{l^*}{2} \right]. \end{aligned} \tag{16}$$

For an *isotropic single-component* fluid, according to the SPT of Boublik *et al.*,^{6–8,10} the parameter ψ in Eq. (13) is given by

$$\psi = \alpha^2. \tag{17}$$

With this form of ψ , the equation of state, Eq. (13), is called ‘‘improved scaled particle theory’’ (ISPT). In the case of hard diatomics ($n=2$) this yields very accurate results for P in comparison with computer simulations, but otherwise the ISPT increasingly overestimates the pressure with increasing n .^{9–11} The alternative version of SPT described by Cotter^{24,25} produces a different result for ψ . Strictly developed for hard spherocylinders, one can show that Cotter’s expression for ψ is

$$\psi = \frac{ds}{9v} \left[3\alpha - \left(\frac{ds}{4v} \right) \right]. \tag{18}$$

Cotter’s work also allows for nematic ordering, on relating α to the nematic-phase B_2 via Eq. (14). The main source of the difference between the two forms of SPT appears to be the fact that Cotter’s version is based on ‘‘two-variable’’ scaling,^{24,25} whereby the molecular diameter and length are scaled independently, whereas Boublik⁷ employs a single scaling parameter for all molecular dimensions. We have found, however, that an expression for ψ similar to that in Eq. (18) follows from the mixture version of Boublik’s SPT³¹ when the latter is applied to the binary-mixture representation of an n -mer fluid discussed in the previous subsection, rather than to the original single-component representation. In this case, one obtains the same expression for pressure as in Eq. (13), with ψ given by³²

$$\psi = \frac{ds}{9v} \left[3\alpha - \left(\frac{ds}{4v} \right) \left(1 - (n-1) \left(\frac{l^*}{2} \right)^2 \right) \right]. \tag{19}$$

(The mixture form of SPT due to Cotter and Wacker²⁵ produces the same result as Eq. (18) for ψ using both the single-

component and binary-mixture representations.) One sees that Eq. (19) agrees with Eq. (18) in the ‘‘spherocylinder limit,’’¹⁹ of an n -mer fluid [$n \rightarrow \infty, l \rightarrow 0, (n-1)l \equiv L \rightarrow$ finite]. It can also be shown that Eq. (19) is equivalent to Eq. (17) in the case of an isotropic diatomic fluid, when Eqs. (15) and (16) are employed. However, for $n > 2$ and any value of $l^* > 0$, one finds that ψ according to Eq. (19) is smaller than the ISPT expression, Eq. (17), and increasingly deviates from the latter as n increases.

In this work, we will evaluate ψ from Eq. (19), with s and v given by the expressions in Eq. (16). Following Cotter’s SPT, the nonsphericity parameter α in Eqs. (13) and (19) will be obtained for both isotropic and nematic phases from Eq. (14) in terms of B_2 , where the latter in turn is calculated from Eq. (11). Although not demonstrated here for lack of space, we have found that the isotropic pressures calculated from this approach are in excellent agreement with computer simulation results^{3,33} for fully flexible tangent n -mers with n as large as 201, having an accuracy comparable to that of GFD theory.

Using the thermodynamic relation $PN = \rho^2 (\partial F / \partial \rho)_{N,T}$, where any dependence of $f(\{\omega\})$ (and hence of the parameters α and ψ) on density ρ is ignored while taking the ρ -derivative, since $f(\{\omega\})$ minimizes F , one can verify that the excess free energy consistent with the equation of state, Eq. (13), is

$$\frac{\beta \Delta F}{N} = (\psi - 1) \ln(1 - \eta) + \frac{3\alpha\eta}{(1 - \eta)} + \frac{\psi\eta}{(1 - \eta)^2}. \tag{20}$$

D. Self-consistency equations

Using the approximation, Eq. (11), for B_2 , functional minimization of Eq. (1) subject to the normalization condition $\int d\{\omega\} f(\{\omega\}) = 1$ leads to the self-consistency equation

$$f(\{\omega\}) = \frac{1}{Z} \exp \left[-\beta U(\{\omega\}) - \frac{a(\eta)}{(n-1)} \sum_{i=1}^{n-1} \Phi(\omega_i) \right], \tag{21}$$

where Z is the appropriate normalization factor,

$$Z = \int d\{\omega\} \exp \left[-\beta U(\{\omega\}) - \frac{a(\eta)}{(n-1)} \sum_{i=1}^{n-1} \Phi(\omega_i) \right], \tag{22}$$

the function $\Phi(\omega)$ is given by

$$\Phi(\omega) = \frac{(n-1)^2}{v} \int d\omega' f^{(2)}(\omega') v_e^{(2)}(\theta_{\omega\omega'}), \tag{23}$$

and $a(\eta) = (\beta/N) (\partial \Delta F / \partial B_2^*)_\eta$. Using Eqs. (14), (19), and (20), we have

$$a(\eta) = \frac{ds}{9v} \left[\ln(1 - \eta) + \frac{\eta}{(1 - \eta)^2} \right] + \frac{\eta}{(1 - \eta)}. \tag{24}$$

Note that the full self-consistency is achieved by combining Eq. (21) to Eq. (23) with Eq. (12). Note also that only a single type of ‘‘effective potential’’ $\Phi(\omega)$ occurs, but in Eq. (21) this is summed over all bonds of the chain molecule. Due to the combined self-consistency conditions and the in-

tramolecular bonding constraints imposed by $U(\{\omega\})$, the approximations embodied in Eqs. (12) and (21) to Eq. (23) include partial correlations between different bonds of the chain in a nematic phase.

In the rigid-molecule limit, all dimer segments must lock into the same orientation, and hence the intramolecular potential $U(\{\omega\})$ should approach the form

$$e^{-\beta U(\{\omega\})} \propto \prod_{i=1}^{n-2} \delta(\omega_{i+1} - \omega_i). \quad (25)$$

Removing this delta-function factor from Eq. (21), the residual angular probability $f(\omega)$ satisfies

$$f(\omega) = \frac{1}{Z} \exp[-a(\eta) \Phi(\omega)], \quad (26)$$

where $\Phi(\omega)$ is given by Eq. (23) with the identification $f^{(2)}(\omega) \equiv f(\omega)$ in this limit. In the nematic director axis frame, the functions $f(\omega) = f(\theta)$ and $\Phi(\omega) = \Phi(\theta)$ depend only on the polar angle θ with respect to the nematic director. In the case of rigid n -mers, the self-consistency Eq. (26) for a nematic phase was solved by iteration using the same numerical methods described in Sec. II C of Ref. 19 (see also below). All angular integrations such as in Eq. (23) were performed by the trapezoid rule using fine grids for the angular variables θ and ϕ . The function $v_e^{(2)}(\theta_{12})$ is given by Eqs. (6) and (7) for $n=2$, with $v_c^{(2)}(\theta_{12})$ obtained from the appendix of Ref. 19.

In the case of semiflexible n -mers, we have used an intramolecular bond-bending potential^{17,22,23}

$$\beta U_B(\{\omega\}) = -\epsilon \sum_{i=1}^{n-2} \cos \theta_{i,i+1}, \quad (27)$$

where $\theta_{i,i+1}$ is the angle between bonds i and $i+1$. In principle, the total intramolecular potential $U(\{\omega\})$ consists of U_B plus hard-sphere interactions between nonadjacent monomers on a chain. In this case, we solve the self-consistency Eqs. (12) and (21)–(23) by an iteration method analogous to that used for rigid n -mers. That is, starting with a trial guess for the dimer probability $f^{(2)}(\theta)$, the effective potential $\Phi(\theta)$ is evaluated from Eq. (23) on a fine grid of θ values, which is used in Eqs. (21) and (22) to calculate $f(\{\omega\})$ for arbitrary n -mer conformations, and a new estimate of $f^{(2)}(\theta)$ is then determined from Eq. (12). Of course, the last step involves integration over all possible chain conformations. Similar to other work,³⁴ we have carried this out using Monte Carlo methods to generate $\approx 10^6$ self-avoiding chain conformations distributed according to the Boltzmann weight $\exp[-\beta U_B(\{\omega\})]$. These conformations are generated once and stored for repeated evaluation of $f^{(2)}(\theta)$ from Eq. (12) at successive iterations. (In practice, for the values of ϵ considered in this work, explicit checks for chain self-avoidance due to hard-sphere interactions between nonadjacent monomers were unnecessary, since conformations with sufficient back-folding of a chain to produce such interactions had negligible probability.)

Finally, we recall that the pressure of the fluid is given by Eq. (13) with α and ψ determined from B_2 using Eqs. (14) and (19). The equilibrium value of the free energy F is

obtained from Eqs. (1) and (20) with $f(\{\omega\})$ given by Eq. (21). The corresponding chemical potential μ , which along with P is needed in determining the N – I phase coexistence boundaries, can be obtained from the thermodynamic relation $\mu = F/N + P/\rho$. This gives

$$\beta \mu = \ln \left(\frac{\Lambda \rho}{Z} \right) - 1 - a(\eta) \int d\omega \Phi(\omega) f^{(2)}(\omega) + \frac{\beta P}{\rho} + \frac{\beta \Delta F}{N}. \quad (28)$$

The N – I coexistence conditions are obtained by equating P and μ for the two phases.

III. RESULTS

A. Rigid n -mers

We first examine the predictions of the present theory for rigid linear molecules, containing either tangent ($l^* = 1$) or fused ($l^* < 1$) hard spheres. Figures 1(a) and 1(b) show the reduced pressure $P^* \equiv P v_n / kT$ vs. volume fraction η for tangent 8-mers and 20-mers, respectively, comparing the present theory with Monte Carlo simulation data of Yethiraj and Fynnewer²² and with results obtained by these authors in Ref. 17 using the Parsons–Lee decoupling approximation. For both theories, the location of the first-order I – N transition with its accompanying discontinuity in density is indicated by a horizontal line. In comparison with our earlier theory,¹⁹ it is found that the current theory yields a significantly more accurate variation of pressure with density. The present theory also agrees better with the simulation results than the Parsons–Lee theory (especially in the case $n=8$), the latter tending to underestimate the values of P^* for given η .

Figures 2(a) and 2(b) depict the orientational order parameter S_2 vs. η for linear tangent 8-mers and 20-mers, respectively, where S_2 is defined as

$$S_2 = \int d\omega f(\omega) P_2(\cos \theta), \quad (29)$$

P_2 being the second Legendre polynomial. At equilibrium, $S_2 = 0$ in an isotropic phase while it jumps to a positive value in the nematic phase. For the 8-mer case, the present theory slightly overestimates and the Parsons–Lee theory underestimates S_2 in comparison with the MC data²² [which are obtained from both the canonical (NVT) and isobaric-isothermal (NPT) ensembles], while our earlier theory¹⁹ gives almost exact agreement. For 20-mers, in contrast, the present theory is seen to yield nearly exact agreement with the MC results.

The values of the coexisting volume fractions, pressure, and order parameter S_2 in the nematic phase at the I – N transition are listed in Table I. For 8-mers, the present theory underestimates the values of the pressure and densities in both phases while overestimating the magnitude of the density gap, in comparison with MC. These trends change to a slight overestimate of the pressure and density values while giving close agreement for the density gap in the case of 20-mers. For both n -mer cases, the Parsons–Lee theory over-

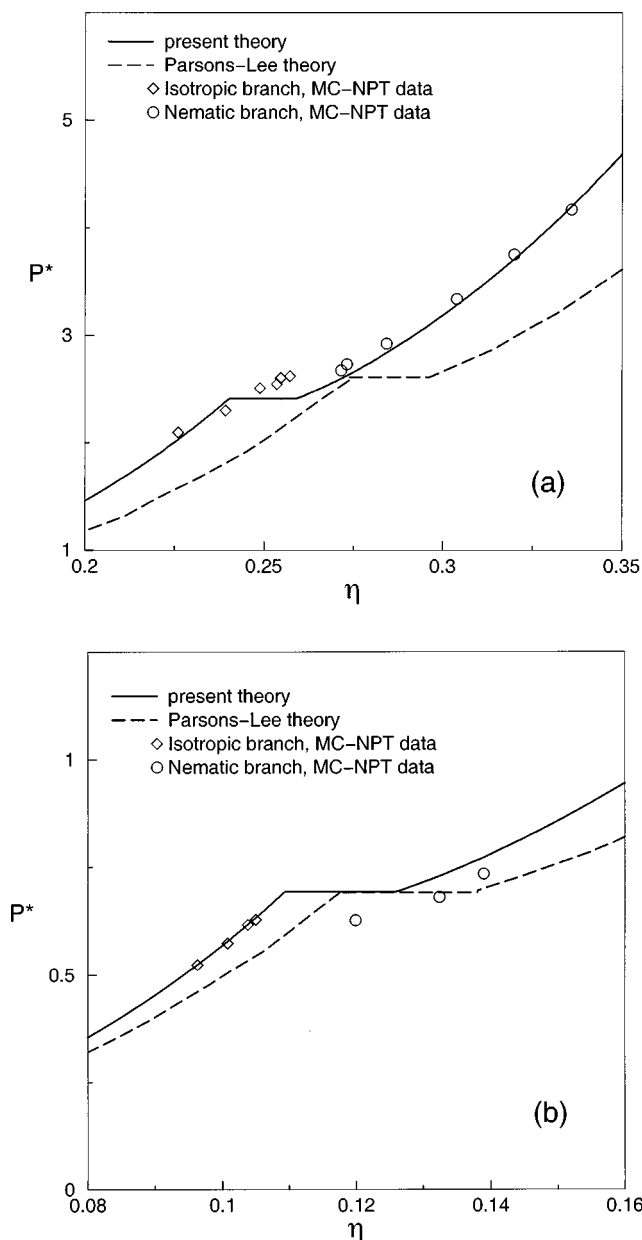


FIG. 1. Variation of the reduced pressure with volume fraction η , comparing the present theory with the Parsons–Lee theory and Monte Carlo data (Ref. 17, 22), for linear tangent 8-mer chains (a) and 20-mer chains (b).

estimates both the value of the densities and the density gap. Table I also includes our results for tangent 7-mers in comparison with MC simulation data and theoretical calculations by Williamson and Jackson¹⁶ using both the Parsons–Lee decoupling approach and a variant of this approach proposed by Vega and Lago.¹⁵ Similar trends to those obtained for 8-mers are seen. At all volume fractions η , the pressures predicted by the present theory and the Vega–Lago theory as implemented in Ref. 16 are in close agreement, but the latter yields a greater underestimate of the transition densities. Finally, Table I includes coexistence results obtained from a recently proposed “modified Parsons–Lee” theory,¹⁸ which replaces the n -mer molecular volume v in the original Parsons–Lee theory by a slightly larger effective volume. The results of this theory improve on those of the Parsons–

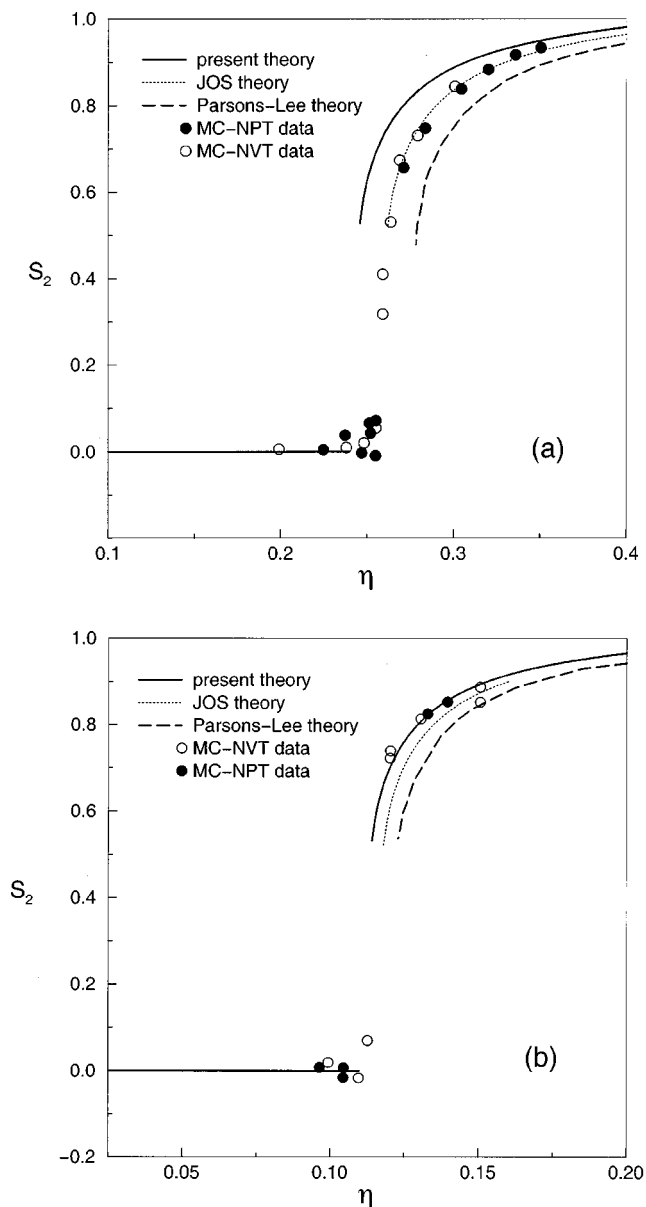


FIG. 2. Variation of the order parameter S_2 with volume fraction η for the same cases as in Fig. 1(a) and 1(b). Also shown are results (denoted JOS) from Ref. 19.

Lee theory and are comparable to the present theory for smaller elongations, but more strongly overestimate the nematic pressure as a function of η in the case of 20-mers.

The only simulation data for the I – N transition in fused hard-sphere n -mers of which we are aware is that due to Whittle and Masters.³⁵ Figures 3(a) and 3(b) compare our present results for P^* vs. η with the simulation data in the case of linear fused 8-mers with reduced bondlength $l^* = 0.5$ and 0.6 , respectively. As in Ref. 19, we also compare with theoretical predictions obtained in Ref. 5 based on GFD theory, which is limited to describing isotropic phases. For the smaller elongation $l^* = 0.5$, both the present theory and our previous one¹⁹ predict the occurrence of an I – N transition at volume fractions between 0.4 and 0.5 (see also Table I), in apparent disagreement with the simulations, which found no unambiguous evidence for such a transition. Oth-

TABLE I. Nematic–isotropic coexistence results for rigid n -mers.

n -mer chain	Source	$\eta(I)$	$\eta(N)$	$S_2(N)$	P^*
7-mer, $l^* = 1.0$	Present theory	0.268	0.286	0.72	2.98
	JOS theory ^a	0.290	0.299	0.649	4.94
	MC-NPT data ^b	0.285 ± 0.018	0.299 ± 0.014	0.64–0.70	3.47 ± 0.32
	Vega–Lago theory ^b	0.255	0.273	≈ 0.7	2.78
	Parsons–Lee theory ^b	0.303	0.319	≈ 0.7	3.12
8-mer, $l^* = 1.0$	Modified Parsons–Lee ^c	0.294	0.313	0.71	3.67
	Present theory	0.240	0.259	0.73	2.41
	JOS theory ^a	0.260	0.269	0.654	3.95
	MC-NPT data ^d	0.257	0.271	≈ 0.7	2.65
	Parsons–Lee theory ^c	0.274	0.295	≈ 0.7	2.61
20-mer, $l^* = 1.0$	Modified Parsons–Lee ^c	0.263	0.283	0.72	2.91
	Present theory	0.109	0.126	0.77	0.692
	JOS theory ^a	0.116	0.124	0.695	0.97
	MC-NPT data ^d	0.105	0.120	≈ 0.7	0.62
	Parsons–Lee theory ^c	0.117	0.137	≈ 0.75	0.69
8-mer, $l^* = 0.5$	Modified Parsons–Lee ^c	0.115	0.134	0.77	0.78
	Present theory	0.423	0.440	0.68	7.13
	JOS theory ^a	0.469	0.477	0.617	13.1
	Present theory	0.378	0.396	0.69	5.42
8-mer, $l^* = 0.6$	JOS theory ^a	0.417	0.425	0.622	9.8

^aReference 19.^bReference 16.^cReference 18.^dReference 22.^eReference 17.

erwise, the simulated pressures at large η lie between the isotropic and nematic branches of the current theory. For the larger elongation $l^* = 0.6$, the simulations³⁵ did show evidence of a transition, indicated by the two distinct branches of P^* vs. η [Fig. 3(b)]. However, since both branches occur over a significant range of pressures, the precise location of the equilibrium transition in the simulation data is uncertain. It is apparent from Fig. 3(b) that the current theory still significantly overestimates the pressure in the nematic region compared with the MC data. Nonetheless, in view of equilibration problems and uncertainties due to finite-size effects, as discussed in Ref. 35, further simulation studies of this fused-chain model would be useful.

B. Semiflexible n -mers

In this subsection, we compare our theory with MC data obtained by Yethiraj and Fynnewer²² as well as with calculations done by the latter authors¹⁷ using the Khokhlov–Semenov (KS) theory²⁶ and a theory based on the Parsons–Lee decoupling approximation with B_2 treated as described at the end of Sec. II A (which will be denoted FY in the following). To indicate the degree of orientational order, we define the order parameter S_2 in the case of semiflexible n -mers by analogy to Eq. (29),

$$S_2 = \int d\{\omega\} f(\{\omega\}) P_2[\cos \theta(\{\omega\})], \quad (30)$$

where $\theta(\{\omega\})$ is now the angle between the nematic director and the *end-to-end* vector of a chain molecule in conformation $\{\omega\}$. This definition of S_2 is comparable to but simpler to evaluate than that used by FY, which relates the “molecular axis” to the eigenvector corresponding to the smallest eigenvalue of the molecular moment of inertia tensor.

Figures 4(a) and 4(b) show the reduced pressure vs. η for semiflexible tangent 8-mers and 20-mers, respectively, for a value of the reduced chain bending energy $\epsilon = 50$. Also shown are MC data and the predictions of the FY and KS theories. It is clear for both n -mers that the present theory improves on both the FY and KS theories, and yields particularly good agreement with MC data for both the isotropic and nematic branches in the case of 20-mers. For 8-mers, however, the pressure of the nematic branch remains significantly underestimated by the present theory, as are the values of the coexisting densities at the I – N transition. Related trends are observed in the behavior of S_2 vs. η for these cases, as shown in Figs. 5(a) and 5(b). For 8-mers, the present theory is seen to overestimate S_2 at any value of η in the nematic phase as well as predict ordering to occur at too low values of η , in comparison with the MC results, while the FY and KS theories produce the opposite behavior. For 20-mers, on the other hand, the present theory yields excellent agreement with the MC data for S_2 . The precise transition values of various quantities are listed in Table II.

The dependence of the order parameter on chain stiffness ϵ in the case of 8-mers at fixed volume fractions $\eta = 0.30$ and 0.35 is shown in Figs. 6(a) and 6(b), respectively. The results are compared with simulation data,²² KS theory (which does not predict nematic ordering at the lower density $\eta = 0.30$), and FY theory.¹⁷ An analogous comparison for 20-mers at $\eta = 0.20$ is shown in Fig. 7. These graphs reveal the obvious qualitative trends that nematic ordering is favored by increasing the stiffness parameter ϵ and that the “critical” value of ϵ for the onset of ordering is reduced on increasing η at fixed n . In the case of 8-mers, the present theory clearly overestimates S_2 as a function of ϵ and underestimates the critical value of ϵ , effects which are more pro-

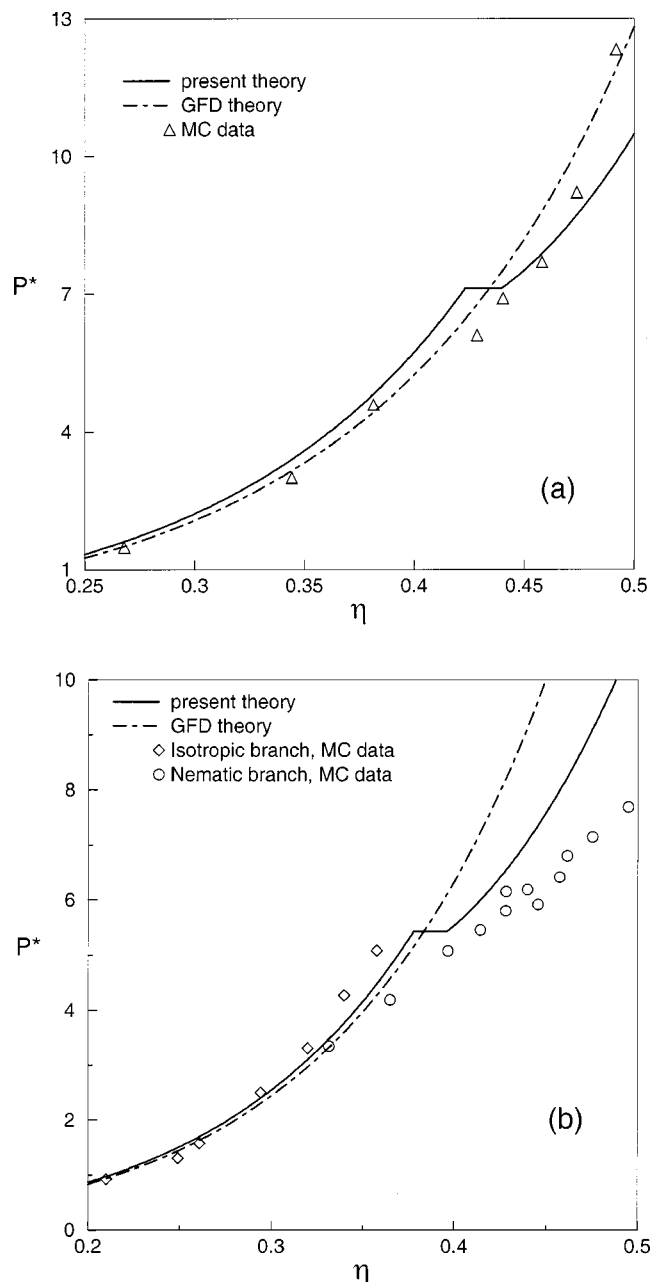


FIG. 3. Variation of the reduced pressure with volume fraction η , comparing the present theory with GFD theory (Ref. 5) and with Monte Carlo data (Ref. 35), for linear fused 8-mers with reduced bondlength $l^* = 0.5$ (a) and $l^* = 0.6$ (b).

nounced at the lower density $\eta = 0.30$ [Fig. 6(a)]. The FY theory errs in the opposite sense. At the higher density $\eta = 0.35$, both the present and FY theory agree more closely with the MC data [Fig. 6(b)], the FY theory giving a better fit. For 20-mers (Fig. 7), the present theory clearly gives the best agreement with MC results for S_2 .

Some additional results indicating effects of chain length and chain stiffness on transition properties are contained in Table II, for 8-mers with $\epsilon = 10$ and 16-mers with $\epsilon = 10, 50$, and 100. The latter cases include comparison with MC results for the coexisting volume fractions obtained by Escobedo and de Pablo.²³ As noted in previous works,^{17,23} all methods agree in predicting that the coexistence densities

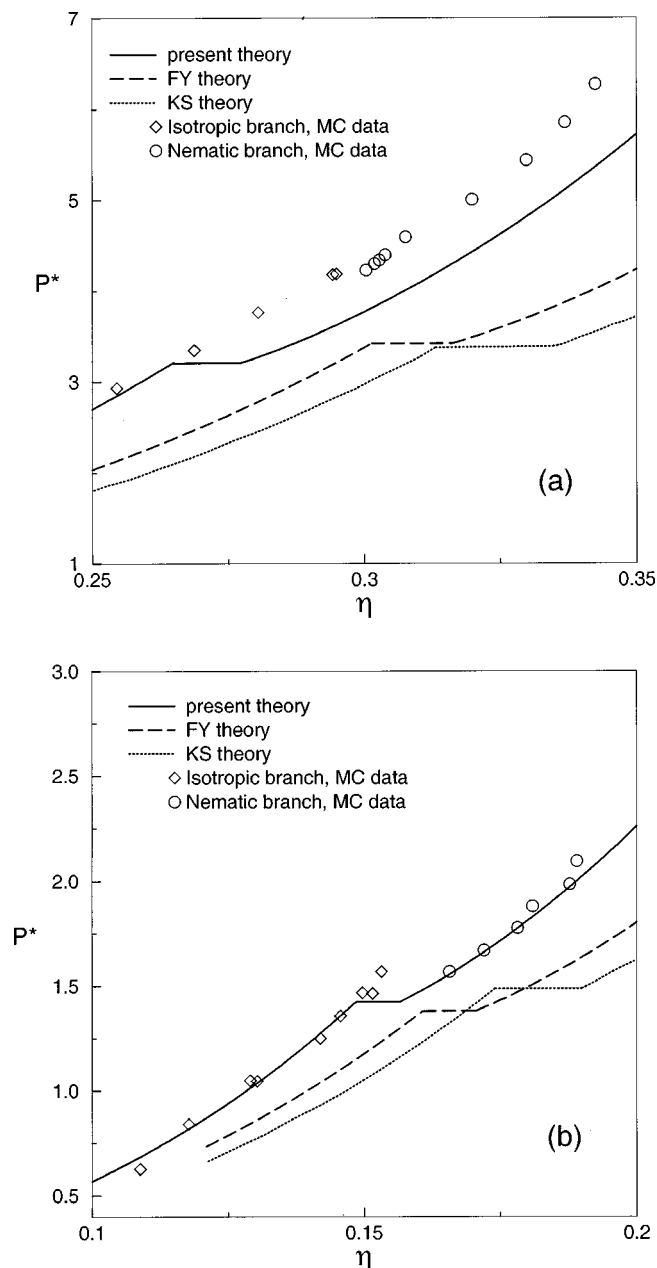
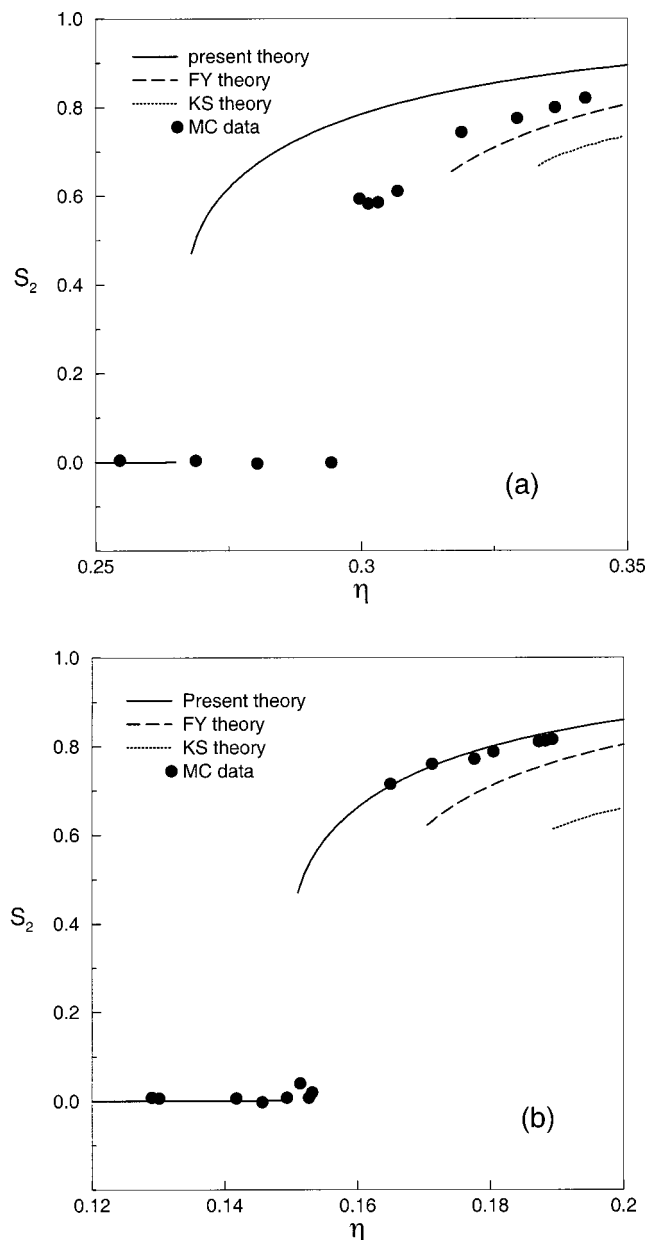


FIG. 4. Reduced pressure vs. volume fraction for semiflexible tangent 8-mers (a) and 20-mers (b) with bending energy $\epsilon = 50$, comparing the present theory with KS theory and Monte Carlo data (Refs. 17, 22).

increase while the density gap $\eta(N) - \eta(I)$ decreases with decreasing chain stiffness ϵ . Increasing the chain length from $n = 8$ to $n = 16$ lowers the volume fractions while increasing the density gap at any given ϵ . Consistent with our other findings, it is seen that the present theory underestimates the coexisting densities in comparison with MC data, whereas those densities are overestimated by both the FY and KS theories.

IV. SUMMARY AND DISCUSSION

For rigid tangent n -mer chains, we have shown that the present theory is in very good agreement with MC simulation data for the density dependence of the pressure and orientational order parameter S_2 as well as for the values of the

FIG. 5. Order parameter S_2 vs. η for the same cases as in Fig. 4(a) and 4(b).

coexisting densities at the $I-N$ transition. The results in these cases improve upon those of our earlier theory,¹⁹ especially for the pressure as a function of density, as well as those of the Parsons–Lee theory and several modified versions^{15,18} of the latter theory. In the case of fused (nontangent) hard-sphere rods, the present theory still shows significant differences from the limited available MC data, and further studies of fused-chain models by both theory and simulation would be worthwhile.

The results of the theory in comparison with MC data for semiflexible tangent hard-sphere chains are mixed. For 8-mers with a fairly strong bending energy $\epsilon=50$, the present theory underestimates the pressure in the nematic phase as well as the values of the coexisting densities at the $I-N$ transition. These effects are related to the finding that the theory overestimates the degree of orientational order S_2 as a function of density in this case. In contrast, very good

TABLE II. Nematic–isotropic coexistence results for semiflexible tangent n -mers.

n -mer chain	Source	$\eta(I)$	$\eta(N)$	$S_2(N)$	P^*
8-mer, $\epsilon=50$	Present theory	0.265	0.277	0.64	3.21
	MC-NPT data ^a	0.294	0.300	≈ 0.6	4.2
	FY theory ^b	0.301	0.316	0.65	3.42
	KS theory ^b	0.313	0.334	0.67	3.38
20-mer, $\epsilon=50$	Present theory	0.149	0.157	0.62	1.43
	MC-NPT data ^a	0.153	0.166	0.72	1.57
	FY theory ^b	0.161	0.171	0.62	1.38
8-mer, $\epsilon=10$	Present theory	0.174	0.190	0.62	1.49
	FY theory ^b	0.344	0.352	0.61	7.57
	KS theory ^b	0.380	0.388	na	na
16-mer, $\epsilon=10$	Present theory	0.412	0.428	na	na
	FY theory ^b	0.284	0.292	0.64	7.36
	KS theory ^b	0.311	0.316	na	na
16-mer, $\epsilon=50$	Present theory	0.344	0.362	na	na
	MC data ^c	0.169	0.179	0.63	1.65
	FY theory ^b	0.176	0.187	na	na
	KS theory ^b	0.184	0.196	na	na
16-mer, $\epsilon=100$	Present theory	0.198	0.216	na	na
	MC data ^c	0.152	0.164	0.66	1.26
	FY theory ^b	0.158	0.173	na	na
	KS theory ^b	0.166	0.179	na	na
		0.177	0.197	na	na

^aReference 22.^bReference 17.^cReference 23.

agreement with simulation data is obtained for 20-mer chains. These differences between the predictions of the theory for 8-mers and 20-mers are similar to but much more pronounced than found in the case of rigid n -mers. Similarly, we find that the present theory overestimates the degree of order as a function of the chain bending energy ϵ at fixed density and underestimates the bending energy required for the onset of ordering in the case of 8-mers, but agrees very well with simulation data for 20-mers.

The underestimation of the density and bending energy required for nematic ordering, more pronounced for shorter chains, are in contrast with trends exhibited by both the FY (Ref. 17) and KS (Ref. 26) theories. The differences between the present theory and that of FY for semiflexible chains reside both in the treatment of the intermolecular excluded volume and the evaluation of density-dependent factors in the excess free energy. Note that for rigid chains, the FY theory reduces to the Parsons–Lee theory, which we have shown to be less accurate than the present theory. On the other hand, the FY theory approximately takes account of chain flexibility in evaluating the excluded volume (see Sec. II A) and is expected to be more accurate in that regard. The present treatment of the excluded volume of two chains is more closely related to that of KS theory, although, as described in Sec. II B, for the latter purpose KS theory represents segments of the chain molecule by spherocylinders rather than by dimers, which is one factor contributing to the quantitative differences between these theories. Another factor which is known^{36,37} to produce overestimates of the densities required for nematic ordering by KS theory (as implemented in Refs. 17 and 22) is its use of the Onsager²⁷ trial form for the orientational distribution function. The fact that

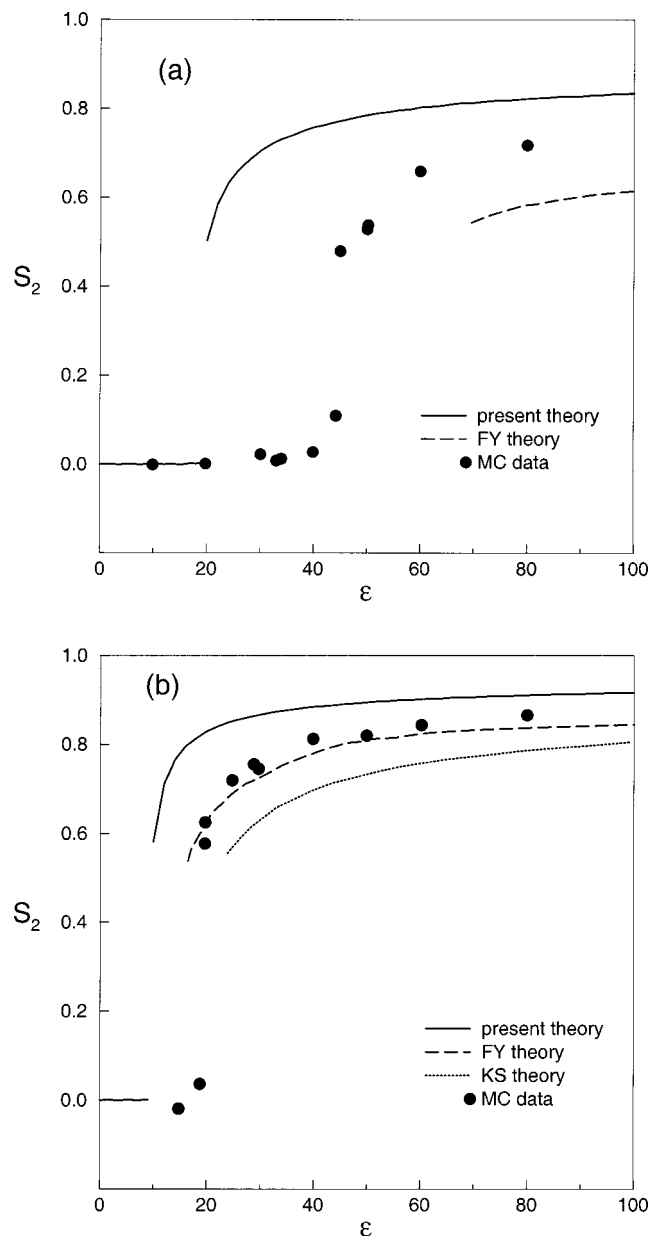


FIG. 6. Variation of S_2 with bending energy ϵ for semiflexible tangent 8-mers at volume fraction $\eta=0.30$ (a) and $\eta=0.35$ (b), comparing the present theory with KS theory, FY theory, and Monte Carlo data (Refs. 17, 22).

the present theory *overestimates* the degree of orientational ordering and hence underestimates the density or bond-bending energy required for the onset of ordering is explained by its approximate treatment of the excluded volume and second virial coefficient B_2 in Eq. (11). For semiflexible chains, that approximation overcounts the excluded volume because it neglects simultaneous contacts between a pair of molecules at two or more separate points along the chains. This overestimation of the excluded volume, which increases with chain length n , is more pronounced in an isotropic phase, since the average conformations of chains in a nematic phase are more “rod-like” and hence more accurately described by the approximation, Eq. (11). Therefore the present theory overestimates the difference in translational entropy between the isotropic and nematic phases, which ac-

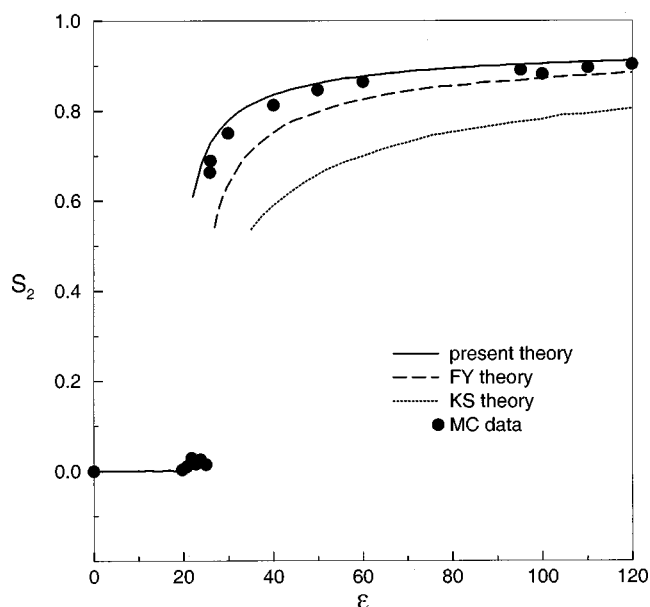


FIG. 7. Same as Fig. 6, for semiflexible tangent 20-mers at volume fraction $\eta=0.20$.

counts for overestimating the degree of orientational order.

The fact that the approximation Eq. (11) overestimates the pair excluded volume and therefore B_2 in an isotropic phase of semiflexible chain molecules implies that the accuracy of the theory in predicting the pressure vs. density of flexible ($\epsilon=0$) tangent n -mers with large n , mentioned in Sec. II D, must be due to a cancellation of errors at high densities. A similar cancellation of errors has been noted previously in connection with GFD theory.³⁸ This effect may explain why the present theory for the N – I transition properties of semiflexible n -mers appears to be more accurate at larger n .

In summary, we have taken several steps toward developing a quantitative first-principles theory of nematic ordering in athermal chain fluids, both rigid and semiflexible. Further studies are required to address the inaccuracies of the theory noted above, especially in characterizing the behavior of rigid fused hard-sphere chains and overestimating the orientational order of semiflexible chains with small n . In the latter connection, it would be of interest to seek systematic corrections to the monomer–dimer representation of the chain excluded volume. Other directions for future study include extending the theory to other molecular architectures and to models of thermotropic liquid crystals.

ACKNOWLEDGMENTS

This work was supported by a research grant from the Natural Sciences and Engineering Research Council (Canada), and by a NATO Collaborative Research Grant. The authors wish to thank A. Yethiraj for several helpful comments and for providing results of the theory in Ref. 17.

¹M. S. Wertheim, J. Chem. Phys. **87**, 7323 (1987).

²W. G. Chapman, G. Jackson, and K. E. Gubbins, Mol. Phys. **65**, 1057 (1988).

³K. G. Honnell and C. K. Hall, J. Chem. Phys. **90**, 1841 (1989).

- ⁴L. A. Costa, Y. Zhou, C. K. Hall, and S. Carra, *J. Chem. Phys.* **102**, 6212 (1995).
- ⁵S. D. Mehta and K. G. Honnell, *J. Phys. Chem.* **100**, 10408 (1996).
- ⁶T. Boublik and I. Nezbeda, *Chem. Phys. Lett.* **46**, 315 (1977).
- ⁷T. Boublik, *Mol. Phys.* **44**, 1369 (1981).
- ⁸T. Boublik, *Mol. Phys.* **68**, 191 (1989).
- ⁹J. M. Walsh and K. E. Gubbins, *J. Phys. Chem.* **94**, 5115 (1990).
- ¹⁰T. Boublik, C. Vega, and M. Diaz-Pena, *J. Chem. Phys.* **93**, 730 (1990).
- ¹¹Y. Zhou, C. K. Hall, and G. Stell, *J. Chem. Phys.* **103**, 2688 (1995).
- ¹²S. Sen, J. M. Cohen, J. D. McCoy, and J. G. Curro, *J. Chem. Phys.* **101**, 9010 (1994).
- ¹³A. Yethiraj and C. E. Woodward, *J. Chem. Phys.* **102**, 5499 (1995).
- ¹⁴C. N. Patra and A. Yethiraj, *J. Chem. Phys.* **112**, 1579 (2000).
- ¹⁵C. Vega and S. Lago, *J. Chem. Phys.* **100**, 6727 (1994).
- ¹⁶D. C. Williamson and G. Jackson, *J. Chem. Phys.* **108**, 10294 (1998).
- ¹⁷H. Fynewever and A. Yethiraj, *J. Chem. Phys.* **108**, 1636 (1998).
- ¹⁸S. Varga and I. Szalai, *Mol. Phys.* **98**, 693 (2000).
- ¹⁹K. M. Jaffer, S. B. Opps, and D. E. Sullivan, *J. Chem. Phys.* **110**, 11630 (1999).
- ²⁰J. D. Parsons, *Phys. Rev. A* **19**, 1225 (1979).
- ²¹S. D. Lee, *J. Chem. Phys.* **87**, 4972 (1987).
- ²²A. Yethiraj and H. Fynewever, *Mol. Phys.* **93**, 693 (1998).
- ²³F. A. Escobedo and J. J. de Pablo, *J. Chem. Phys.* **106**, 9858 (1997).
- ²⁴M. A. Cotter, *J. Chem. Phys.* **66**, 1098 (1977).
- ²⁵M. A. Cotter and D. C. Wacker, *Phys. Rev. A* **18**, 2669 (1978).
- ²⁶A. R. Khokhlov and A. N. Semenov, *Physica A* **108**, 546 (1981); **112**, 605 (1982).
- ²⁷L. Onsager, *Ann. N.Y. Acad. Sci.* **51**, 627 (1949).
- ²⁸D. C. Williamson and G. Jackson, *Mol. Phys.* **86**, 819 (1995).
- ²⁹N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**, 635 (1969).
- ³⁰We will assume that the intramolecular hard-sphere interactions are such that only conformations $\{\omega\}$ which do not produce overlap of nonadjacent monomers are allowed. Then the expression in Eq. (16) for s_n and v_n apply to both rigid and semiflexible molecules (Ref. 10). Note that some other models of semiflexible fused hard-sphere chain molecules allow for overlap between certain pairs of nonadjacent monomers (Refs. 4,9).
- ³¹T. Boublik, *Mol. Phys.* **27**, 1415 (1974); *J. Chem. Phys.* **63**, 4084 (1975).
- ³²Note that the relations, Eq. (10), for x_1 and x_2 are consistent with conservation of the total number of atomic sites (since $x_1 + 2x_2 = n$) as well as of molecular volume v_n , surface area s_n , and mean radius of curvature r_n : one can trivially verify that $v_n = x_1 v_1 + x_2 v_2$, $s_n = x_1 s_1 + x_2 s_2$ and $r_n = x_1 r_1 + x_2 r_2$ using the expressions for v_n , s_n , and r_n given in Eq. (16).
- ³³J. Gao and J. H. Weiner, *J. Chem. Phys.* **91**, 3168 (1989).
- ³⁴M. Muller and M. Schick, *Phys. Rev. E* **57**, 6973 (1998).
- ³⁵M. Whittle and A. J. Masters, *Mol. Phys.* **72**, 247 (1991).
- ³⁶Z. Y. Chen, *Macromolecules* **26**, 3419 (1993).
- ³⁷M. Dijkstra and D. Frenkel, *Phys. Rev. E* **51**, 5891 (1995).
- ³⁸A. Yethiraj, K. G. Honnell, and C. K. Hall, *Macromolecules* **25**, 3979 (1992); A. Yethiraj, *J. Chem. Phys.* **102**, 6874 (1995).