PHYSICAL REVIEW A VOLUME 28, NUMBER 6 DECEMBER 1983

Ordered phases of rigid cores having semiflexible tails. II. Model for smectic-*A* and reentrant-nematic phases with hard repulsions

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(Received 2 November 1982; revised manuscript received 1 August 1983)

The general partition function of the preceding paper is applied to the special cases of smectic-*A* and nematic liquid crystals and isotropic liquids in bulk phases. The relative stabilities of the isotropic, nematic, smectic-*A*, and reentrant-nematic phases are studied as a function of temperature, pressure, tail flexibility, and tail length. The following thermodynamic and molecular ordering properties are studied in these phases and at the phase transitions: smectic-*A* order parameter, core and tail intermolecular orientational order parameters, tail intramolecular orientational order parameter, density, and entropy. The role of the semiflexible tails in stabilizing the smectic-*A* and reentrant-nematic phases is explicitly elucidated.

INTRODUCTION

The general partition function presented in the preceding paper[1] for molecules composed of rigid cores with semiflexible tails and interacting via site-site (segmental) hard repulsions is applied in this paper to the special case of the smectic-*A* liquid crystal, in which the molecules have some positional ordering in one dimension of the system and also have some orientational order. That is, the long molecular axes of the molecules tend to align parallel to a preferred axis of orientation in the system, and the molecules tend to arrange themselves into layers, in which the plane of each layer is perpendicular to the preferred axis of orientation. There is liquidlike positional disorder *within* each layer.

The smectic-*A* partition function of this paper can be applied to systems of two dimensions (films) and of three dimensions (bulk phases). This partition function can be reduced to the partition function[2] for the nematic liquid crystal when the smectic-*A* order parameter goes to zero and can be reduced to the partition function for the isotropic liquid when both the smectic-*A* order parameter and the nematic (orientational) order parameter go to zero.

Other models[3–16] that treat both smectic-*A* and nematic phases have been interesting and useful. However, these models (which for the most part have been rather phenomenological in approach) have *not* focused explicitly on the flexibility of the tail chains of the molecules and thus on the effect of the excluded volumes (packing) of these *semi*flexible tail chains on the relative stabilities of the isotropic, nematic, smectic-*A*, and reentrant- (low-temperature) nematic phases. (References 17–19 contain some examples of some reentrant-nematic phases.) The lattice model of this paper is unique in that the geometry of a molecule (i.e., the excluded volumes of both the rigid and semiflexible portions of the molecule) can be treated in a rather explicit manner.

Such an explicit treatment is needed to understand better the behavior of real liquid crystals from the standpoint of molecular structure. With very few exceptions,[20,21] real molecules that form *any* kind of smectic (i.e., layered, or positionally ordered) liquid crystalline phase have one or two pendant semiflexible tail chains of significant length; if the tail chain is shortened, the smectic phases disappear.[22] The model of this paper shows that differences in packing between rigid cores and semiflexible tails can, in some ranges of temperature and pressure, force the molecules in the system to form smectic-*A* layers so that cores tend to pack with cores and tails tend to pack with tails.

Furthermore, this model shows that as the tails become more rigid (and rodlike) as the temperature decreases, the segregated packing of the smectic-*A* phase is no longer advantageous and thus disappears, allowing the nematic phase to reappear (reenter) at a temperature below that of the smectic-*A* phase.

The nematic model[2] to which the smectic-*A* model of this paper can be reduced when the smectic-*A* order goes to zero has been very successful in studying the effect of the excluded volumes of the semiflexible tail chains on the relative stabilities of the nematic and isotropic phases. This observation provides a compelling rationale for the development of the general model of the preceding paper[1] and from it, the development of the special smectic-*A* model in this paper.

This paper is the first in a series of future papers dealing explicitly with the effect of the semiflexible tail chains on the smectic-*A* and reentrant-nematic phases. Future papers[23] in this series deal with the added effects (1) of intermolecular site-site (segmental) attractions (arising from London dispersion forces) and soft repulsions, (2) of dipolar interactions (including dipole-dipole and dipole-induced dipole), (3) of the number of tails per core, and (4) (with systems of one-tail molecules) of the molecular tails being parallel (monolayer-type structure) or opposed (bilayer-type structure) in both lattice models and nonlattice models.

In this paper the effects of temperature, pressure, tail-chain flexibility, and tail-chain length on the relative stabilities of the isotropic, nematic, smectic-*A*, and reentrant-nematic phases are explored using a lattice model for bulk phases of molecules having only hard repulsions. Such a model is a base or reference model to which the other molecular features mentioned in the preceding paragraph have been added in later papers[23]; this approach thus provides a method for determining on an individual basis which of these molecular features are sufficient and/or necessary for the existence of smectic-*A* and reentrant-nematic phases and also the relative importance, one with respect to the other, of these features in affecting the relative stabilities of the various phases.

MODEL

General smectic-*A* model

In this model we have an unbranched molecule with a rigid core section and pendant semiflexible tail sections. Each molecule has a total of m segments, with each segment occupying one lattice site. The lattice may be either simple cubic or square planar. The length of the edge of one segment is a_0. There can be unoccupied or empty lattice sites ("holes") in the system. Each molecule has r rigid core segments, f semiflexible tail segments, $(r-1)$ rigid bonds, and f semiflexible tail bonds.

If

$$\lambda_1=\lambda \ , \tag{1a}$$

and

$$\lambda_k=0 \ , \quad k>1 \tag{1b}$$

then the general Ω in Eq. (34) of the preceding paper[1] becomes

$$\Omega=\left[\prod_k[(N_k/2)!]^2\right]^{-1}\prod_{l=R,F}\left\{\left[\left[M_l-[(r-1)+qr\lambda+f\alpha_{11}(1-q\lambda)](N_1/2)-\sum_{k\neq 1}f\alpha_{k1}(N_k/2)\right]!\right]\right.$$
$$\times\left[\prod_{\substack{d=2\\ 1\neq d\neq j\neq 1}}^{Y}\{[M_l-(r-1+f\alpha_{dd})(N_d/2)-f\alpha_{1d}(1-q\lambda)(N_1/2)-f\alpha_{jd}(N_j/2)]!\}\right]$$
$$\left.\times(\{[M_l-m(N/2)-q(r-f)\lambda(N_1/2)]!\}(M_l!)^{(Y-1)})^{-1}\right\} . \tag{2}$$

[Note that the term $f\alpha_{jd}(N_j/2)$ in Eq. (2) is zero for the square-planar lattice.]

In Eq. (2) and later equations in the paper, the following conventions[1] are used: If the subscript l is set equal to R (referring to the R region), then $q=+1$; if the subscript l is set equal to F (referring to the F region), then $q=-1$. All terms (including the ranges for sums and products) not defined in this paper have been previously defined in the preceding paper.[1]

Equation (2) with $0<\lambda\leq 1$ is proper to use for the special case of the smectic-*A* liquid-crystal phase, where axis 1 is the preferred axis of orientation for the long axis of the cores of the molecules. The λ is then a parameter for orientated molecules that denotes the degree of segregation of the rigid segments of these molecules into the R region and also the degree of segregation of the semiflexible segments of these molecules into the F region. Such a segregation of rigid and semiflexible segments gives rise to one smectic-*A* layer, in which the plane of the layer is perpendicular to the preferred axis of orientation. The plane of the R region and the plane of the F region of one layer are perpendicular to the preferred axis of orientation; the stack of layers of a bulk smectic-*A* sample form a stack of alternating R and F regions.

When $\lambda=1$, the boundary planes between the layers (as well as between the regions) are well defined. When $0<\lambda<1$, these boundary planes are less sharply defined, as discussed earlier [see comments following Eq. (16) of Ref. 1].

A smectic-*A* phase exists for any value of $0<\lambda\leq 1$; that is, a smectic-*A* phase exists as soon as there is any degree of segregation of rigid and semiflexible segments of orientationally ordered molecules. That a smectic-*A* phase can exist with small λ's is consistent with experimental results,[16,24] in which many smectic-*A* phases have only a small amount of positional order (layer structure).

For mathematical tractability, we shall focus on the segregation of rigid and semiflexible segments to form a typical layer (i.e., the system here is one layer). We apply periodic boundary conditions to the top and bottom of the layer and ignore correlations between different smectic-*A* layers, an approach consistent with experiment, which reveals little, if any, correlation between molecules in different smectic-*A* layers.[16,24]

With the use of Eq. (33), the number density ρ_l^* in the l region is defined by

$$\rho_l^*=\left[\sum_k N_{lk}\right]\Big/M_l=N/(2M_l) \ , \quad l=R,F \ . \tag{3}$$

The density ρ_l, or the fraction of occupied lattice sites in the l region, is given by

$$\rho_l=[m(N/2)+q(r-f)\lambda(N_1/2)]/M_l \ , \quad l=R,F \tag{4}$$

$$\rho=mN/M \ , \tag{5}$$

where M, the total number of lattice sites in the system, is given by

$$M = M_R + M_F \; . \tag{6}$$

In a lattice model, each molecular segment—whether a rigid core segment or a semiflexible tail segment—has the same volume, i.e., the volume of one lattice site. In this model [see discussions in Ref. 1 following Eqs. (1), (16), and (26)], the segment face at which a molecule crosses from the R region into the F region *defines* the local surface between the two regions. Furthermore, each ρ_l in this model is, for reasons of mathematical tractability, an average density for the l region. Therefore, in this model,

$$\rho_R = \rho_F = \rho \; . \tag{7}$$

If $\rho_R \neq \rho_F$, then there would be some molecules consisting of tails without cores or cores without tails in the system.

In experimental systems observed thus far, the tail segments and core segments do not have exactly the same volumes, and a density wave[16] has been observed along the axis perpendicular to the smectic-A layers. *However*, even though the total ρ_R is equal to the total ρ_F in this model, the rigid and semiflexible segments of a molecule do pack differently in the *different* directions in the different regions of the lattice in the smectic-A phase, as is clear from an inspection of Eqs. (2) and (4) and as is seen in x-ray studies.[16,24]

If $\lambda \neq 0$, then $M_R \neq M_F$ and $\rho_R^* \neq \rho_F^*$. Physically, this statement and Eq. (7) imply that as λ changes (and thus, as the fractions, X_R and X_F, of rigid to semiflexible segments in the R and F regions, respectively, change), the region boundaries shift (and the total number of lattice sites in each region changes) to preserve the equality between ρ_R and ρ_F.

Equations (4)—(7) yield

$$M_l = M\{1 + q[(N_1/N)\lambda(r - f)/m]\}/2 \; , \quad l = R,F \; . \tag{8}$$

A future paper[23] starts with Eqs. (2)—(8) and deals with the molecules of this model in two dimensions (i.e., in films). In the next sections of this paper, the three-dimensional (bulk) case is treated.

Simple-cubic lattice model for smectic-*A*, nematic, and isotropic phases

In this paper, we want to consider a simple-cubic (sc) lattice system with only infinitely hard repulsions between molecular segments. The distribution of rigid cores about axis 1, the preferred axis of orientation for the cores, is assumed to be symmetric. Let

$$s = N_2/N = N_3/N \tag{9a}$$

be the fraction of molecules with core long axes parallel to one of the two nonpreferred axes of orientation of the system, and let

$$(1 - 2s) = N_1/N \tag{9b}$$

be the fraction of molecules with core long axes parallel to the preferred axis. The average orientational order parameter η for a core bond in this sc lattice model is given by

$$\eta = \langle (3\cos^2\theta_s - 1) \rangle /2 = 1 - 3s \; , \tag{10}$$

where θ_s is the angle between the core long axis and the preferred axis of orientation. Clearly, the exact relationships between s, η, and the N_k's in the simple-cubic lattice will be somewhat different from those in the square-planar lattice.[23]

The coupling of the core orientational order parameter η, the smectic-A order parameter λ, and the density ρ of the system arises *naturally* here from the physical description of the *microscopic molecular* behavior in the smectic-A phase. This coupling becomes readily apparent from a consideration of Eqs. (4), (7), (9b), and (10).

The fraction t of semiflexible bonds parallel to one of the nonpreferred axes of orientation for the cores is given by

$$t = u(1 - 2s) + (1 - 2u)s + us = s + u(1 - 3s) \; , \tag{11}$$

where u is given by Eq. (2) of Ref. 1. The fraction of semiflexible bonds parallel to the preferred axis of orientation for the cores is then $(1 - 2t)$. The average *inter*molecular order parameter τ for the semiflexible bonds in this model is given by

$$\tau = \langle (3\cos^2\theta_t - 1) \rangle /2 = 1 - 3t = \eta v \; , \tag{12}$$

where θ_t is the angle between a semiflexible bond and the preferred axis of core orientation, and v is given by Eq. (6) of Ref. 1. (In the isotropic phase, $s = t = \frac{1}{3}$. In the smectic-A and the nematic liquid-crystal phases, $s < \frac{1}{3}$ and $t < \frac{1}{3}$.)

The total configurational Helmholtz free energy A_c for the system is given by

$$\begin{aligned} -A_c/(NkT) &= (\ln Q_c)/N = (\ln\Omega)/N \\ &= \left[\sum_{l=R,F} [(Q_{l1}\ln Q_{l1} + 2Q_{l2}\ln Q_{l2} \right. \\ &\qquad \left. - C_{l1}\ln C_{l1})/(2\rho_l^*)] \right] - C_2 \; , \end{aligned} \tag{13}$$

where

$$Q_{l1} = 1 - \rho_l^*\{(1 - 2s)[(r - 1) + q\lambda C_4] + (1 - 2t)f\} \; , \tag{14}$$

$$Q_{l2} = 1 - \rho_l^*[s(r - 1) + tf - q(1 - 2s)\lambda C_5] \; , \tag{15}$$

$$C_{l1} = 1 - \rho_l^*[m + q(1 - 2s)\lambda(r - f)] \; , \tag{16}$$

$$C_2 = (1 - 2s)\ln(1 - 2s) + 2s\ln s + \sum_{l=R,F} [(\ln\rho_l^*)/2] \; , \tag{17}$$

$$C_4 = r - (1 - 2u)f \; , \tag{18}$$

and

$$C_5 = uf \; . \tag{19}$$

When $\lambda \rightarrow 0$, $\rho_R^* \rightarrow \rho_F^*$; and $(\ln\Omega)/N$ in Eq. (13) reduces to Eq. (II.25) of Ref. 2 appropriate for nematic and isotropic phases.

The thermodynamically stable states of the system at constant T and pressure P (or at constant T and corresponding volume V of the system)[25] correspond to minima in the configurational Gibbs free energy G_c as a function of s and λ:

$$\left[\frac{\partial[G_c(NkT)]}{\partial s}\right]_{P,T,\lambda}=\left[\frac{\partial[A_c(NkT)]}{\partial s}\right]_{\rho_R^*,\rho_F^*,T,\lambda}$$

$$=\left[\sum_{l=R,F}[-(C_3+q\lambda C_4)\ln Q_{l1}+(C_3+2q\lambda C_5)\ln Q_{l2}+q\lambda(r-f)\ln C_{l1}]\right]+2\ln[s/(1-2s)]=0\ , \qquad (20)$$

where

$$C_3=r-1+(1-3u)f\ . \qquad (21)$$

Note that

$$V=Mv_0=Ma_0^3\ , \qquad (22)$$

where v_0 is the volume of a lattice site [i.e., the "hard-repulsion" (steric) volume of one molecular segment]. Also,

$$\left[\frac{\partial[G_c/(NkT)]}{\partial\lambda}\right]_{P,T,s}=\left[\frac{\partial[A_c/(NkT)]}{\partial\lambda}\right]_{\rho_R^*,\rho_F^*,T,s}=(1-2s)\left[\sum_{l=R,F}[qC_4\ln Q_{l1}-2qC_5\ln Q_{l2}-q(r-f)\ln C_{l1}]\right]\Big/2=0\ . \qquad (23)$$

The constraint $0\leq\lambda\leq 1$ is required to hold.

Using the relation $P=-(\partial A_c/\partial V)_T$, one obtains

$$\Phi=\frac{Pv_0}{kT}=\left[\frac{\partial\ln Q_c}{\partial M}\right]_{N,T}$$

$$=\sum_{l=R,F}[(1-C_{l1})(\ln Q_{l1}+2\ln Q_{l2}-\ln C_{l1})/(2\rho_l^* m)]\ . \qquad (24)$$

The configurational chemical potential μ of the system is

$$\frac{\mu}{kT}=-\left[\frac{\partial\ln Q_c}{\partial N}\right]_{M,T}$$

$$=\left[\sum_{l=R,F}\{[(1-Q_{l1})\ln Q_{l1}+2(1-Q_{l2})\ln Q_{l2}-(1-C_{l1})\ln C_{l1}]/(2\rho_l^*)\}\right]+C_2\ . \qquad (25)$$

The configurational entropy S_c of the system is given by

$$\frac{S_c}{Nk}=-\left[\frac{\partial[A_c/(Nk)]}{\partial T}\right]_{M,N}$$

$$=\frac{\ln Q_c}{N}+T\left[\frac{\partial[(\ln Q_c)/N]}{\partial T}\right]_{M,N}$$

$$=\frac{\ln\Omega}{N}+TIf\sum_{l=R,F}[K_l\ln(Q_{l1}/Q_{l2})]\ . \qquad (26)$$

Here,

$$K_l=(1-3s)-q(1-2s)\lambda\ , \qquad (27)$$

and

$$I=\frac{\partial u}{\partial T}=\frac{uE_b}{kT^2(1+2\Lambda)}\ , \qquad (28)$$

where u and Λ are given, respectively, by Eqs. (2) and (3) of Ref. 1. As in earlier papers,[2,26] the term in square brackets in the last line in Eq. (26) arises from the explicit separation of degrees of freedom in the system between internal and configurational.[1] As an approximation, the fraction $2u$ of bent bonds in the chains of the molecules in these models is treated as an internal property (as a function of T at a given bond-bending energy E_b). However, u also appears explicitly in the configurational partition function Q_c, thus contributing the second term in brackets in the last line in Eq. (26).

Using a simplex[27] function-minimization procedure, the appropriate sets of equations from this model were solved numerically by computer calculations to find the thermodynamically stable states of the system under given conditions of temperature and pressure. At the transition between two phases 1 and 2 at a given P and T, $\mu_1=\mu_2$.

When $\lambda=1$, the lower bound on the layer thickness L in this model is equal to d_L, the length of a molecule, where

$$d_L=[r+(1-2u)f]a_0\ , \qquad (29)$$

and where u is given by Eq. (2) of Ref. 1 and a_0 by Eq. (22) of this paper.

When $\lambda\rightarrow 0$, the layer boundaries become increasingly diffuse [see discussions in the three paragraphs preceding Eq. (17) of Ref. 1, and in the paragraphs following Eqs. (26) and (31), Ref. 1], and thus the layer thickness goes to infinity. However, a *practical* upper bound on the layer thickness as $\lambda\rightarrow 0$ is $L=2d_L$. [For practical purposes, when a layer is so thick that there is room to form two separate layers within it, one cannot tell whether one has two layers or one, and thus the integrity of individual layers has been lost. Obviously, this upper bound is only a practical one since the location of the core or tail of one molecule with respect to the cores or tails of other molecules is random when $\lambda\rightarrow 0$ in this model (see abovementioned discussions).]

Using these bounds on L as λ approaches its minimum and maximum values, the following equation for L is derived:

$$L=d_L(2-\lambda)\ . \qquad (30)$$

TABLE I. Thermodynamic and molecular ordering properties for the system in which $r=4$, $f=8$, $E_b/k=250$ K, and $Pv_0/k=43.25$ K.

T (K)	Stable phase	λ	η	τ	ν	ρ
>181.05	I					
181.05	I				0.498 18	0.543 07
	N		0.675 21	0.336 37	0.498 18	0.565 74
180.93	N		0.679 7	0.338 8	0.498 5	0.566 2
	S_A	0.282 6	0.703 3	0.350 6	0.498 5	0.568 2
180.66	S_A	0.200 00	0.700 13	0.349 48	0.499 17	0.568 25
180.47	S_A	0.100 00	0.697 80	0.348 67	0.499 67	0.568 28
180.40	S_A	0.001 00	0.697 03	0.348 40	0.499 84	0.568 28
<180.4	N_R					

RESULTS AND DISCUSSION

The equations of the sc lattice model in the preceding section were solved[28] for smectic-A, nematic, and isotropic phases under various conditions of temperature T, pressure P, tail-chain bond-bending energy E_b, and number f of tail-chain segments; the results from some representative calculations are presented and discussed here.

Nematic, smectic-A, and reentrant-nematic phases

In Tables I and II are presented calculated results for thermodynamic and molecular ordering properties for one system that shows the following sequence of stable phases as a function of *decreasing* temperature: isotropic (I), nematic (N), smectic-A (S_A), and reentrant nematic (N_R).

In the system in Tables I and II, the number r of rigid core segments is 4, f is 8, E_b/k is 250 K, and Pv_0/k is 43.25 K. The value $r=4$ is reasonable compared with length-to-breadth ratios for cores in real liquid crystals[2,29,30]; furthermore, a stable N phase is not observed for rigid rods having an r less than about 3.6 in the sc lattice model with only hard repulsions.[25] Since the purpose of the S_A model of this paper is to elucidate the role of the semiflexible tail chains of liquid-crystal molecules in stabilizing the S_A and N_R phases, we look first at molecules with a significant number of semiflexible tail segments, in particular here, at $f=8$. The value of $E_b/k=250$ K is the approximate lower limit, as estimated from experimental data, for the energy to make a *trans-gauche* bend in a hydrocarbon chain.[2,31] (The approximate upper limit corresponds to $E_b/k=400$ K.) Though both are somewhat small in the particular system studied in Tables I and II, the temperature range over which the higher-T N phase is the most stable phase and that over which the S_A phase is the most stable phase are both significant and real.

TABLE II. Transition properties for the system in which $r=4$, $f=8$, $E_b/k=250$ K, and $Pv_0/k=43.25$ K.

Transition	T (K)	$\Delta\rho/\rho_{\mathrm{mop}}$[a] (%)	$\Delta S_c/(Nk)$
N-I	181.05	4.0063	0.681 94
S_A-N	180.93	0.3487	0.044 87
N_R-S_A	180.4	$0 \leftarrow$	$0 \leftarrow$

[a] "mop" indicates more ordered phase.

As seen in Table I, the *intra*molecular tail orientational order parameter ν increases as T decreases, reflecting the fact that the tails become less flexible and more aligned with the cores to which they are attached, as T decreases. Also, as expected, the density ρ increases as T decreases. In the N phase, the core orientational order parameter η and the *inter*molecular tail orientational order parameter τ increase as T decreases, as expected.[2]

In contrast, η and τ decrease as T and λ decrease in the S_A phase. [As noted after Eq. (10), η is coupled with λ; recall from Eq. (12) that τ is also coupled with η and ν.] As λ decreases, there is less segregated packing in the S_A phase and thus more opportunities for the semiflexible tails to disrupt the orientational order of the cores, thereby decreasing η. The semiflexible tails bend and twist well *around each other,* but tend to disrupt the alignment of the rigid cores. In some T range, one expects λ to decrease in the S_A phase as T decreases (and thus as the transition to the N_R phase is approached).

As seen in Table II, the N-I and S_A-N transitions are weakly first-order transitions, with the relative density change $\Delta\rho/\rho_{\mathrm{mop}}$ and the relative entropy change $\Delta S_c/(Nk)$ about an order of magnitude smaller at the S_A-N transition than at the N-I transition. Experimentally, N-I transitions have always been observed to be weakly first order; S_A-N transitions have in many cases been clearly observed to be weakly first order, while in some cases they have been thought to be essentially second order.[16,22,32,33]

The N_R-S_A transition in Table II appears to be second order; the S_A phase is the stable phase down to at least $\lambda=0.001$, which is the smallest value of λ to which the S_A phase could be pursued with the present computer calculations. As seen in Fig. 1, there is a change in the slope of the plot of ρ vs T as $\lambda \rightarrow 0$, consistent with a second-order transition. The N_R ρ in Fig. 1 appears to extrapolate smoothly from the ρ of the higher-T N phase.

As seen in Table I and Fig. 1, the S_A phase is denser than the N phase at the same T. The partial segregation of different parts of oriented molecules in the S_A phase al-

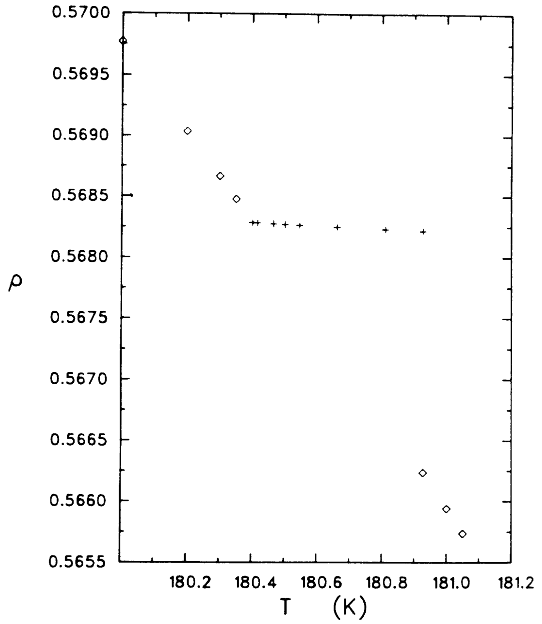

FIG. 1. Density vs temperature in the smectic-*A* phase (plus symbols) and the nematic phases (diamond symbols) in the system in which $r=4$, $f=8$, $E_b/k=250$ K, and $Pv_0/k=43.25$ K.

lows these different parts to pack more efficiently. That is, rigid cores can pack better with other rigid cores, and semiflexible tails can pack better with other semiflexible tails in the ranges of temperature (and pressure) in which the S_A phase is the most stable phase.

At high temperatures, the system density is small enough that the molecules have room to pack isotropically (i.e., with no preferred axis for orientation) and maximize the entropy of the system; hence, the stable I phase. As T decreases, ρ increases, and the molecules must align orientationally at least partially with each other to be able to fit—with the lowest configurational Gibbs free energy G_c—into the available volume V of the system; hence, the stable N phase. In some ranges of temperature, as T decreases further the orientationally-aligned molecules must form at least partially layered structures in order to be able to fit—with lowest G_c—the different parts (shapes) of each molecule into the available volume; hence, the stable S_A phase. As T decreases further, each tail chain becomes increasingly rigid and thus in shape resembles more closely a linear extension of the rigid core to which it is attached; there is then no longer sufficient advantage to the segregated packing of the S_A phase; hence, the stable N_R phase.

As seen by the values of ν in Table I, the tails are certainly not completely rigid, even at the N_R-S_A transition, in this system. The relatively small changes in ν and ρ in each phase between the S_A-N transition and the N_R-S_A transition imply that the relative stabilities of the N and S_A phases are controlled by *small* changes in the density of the system and the flexibility of the tail chains; these factors are in turn controlled by small changes in the temperature and the pressure (as will be seen later) of the system, as well as by changes (as will also be seen later) in the number of tail segments in a molecule and the tail bond-bending energy E_b. Furthermore, the configurational Gibbs free energies of the S_A and N phases at constant T and P in Table I are actually very similar in magnitude, consistent with the experimental observation that differences between the S_A and N phases are small and that the S_A order can be considered to have a somewhat "fragile" existence.[16,24]

The I solution always exists in this model, although the I phase may be metastable with respect to the N and/or S_A solutions at a given T and P. There are ranges of T and P in which both the N solutions and the S_A solutions exist.

In addition to the S_A solutions in Tables I and II, there is also another range of temperatures in which S_A solutions exist. For the system in which $r=4$, $f=8$, and $E_b/k=250$ K, this range is around $T\simeq75$ K. (These low-T S_A solutions have been observed in this system at Pv_0/k values ranging from about 10 to 50 K and may very well exist at other Pv_0/k values.) In this low-T region, λ increases with decreasing T in the S_A phase, which is metastable with respect to the N phase. Furthermore, the differences in G_c between the S_A and N phases at constant T and P are appreciable, especially for larger λ.

TABLE III. Effect of pressure on the thermodynamic and molecular ordering properties for the system in which $r=4$, $f=8$, and $E_b/k=250$ K.

Pv_0/k (K)	T (K)	Stable phase	λ	η	τ	ν	ρ
43.00	> 180.72	I					
	180.72	I				0.499 01	0.542 20
		N		0.675 44	0.337 05	0.499 01	0.564 92
	< 180.72	N					
43.50	> 181.39	I					
	181.39	I				0.49732	0.543 93
		S_A	0.338 27	0.708 78	0.352 49	0.497 32	0.569 37
	180.89	S_A	0.200 00	0.702 83	0.350 42	0.498 59	0.569 42
	180.69	S_A	0.100 00	0.700 49	0.349 60	0.499 09	0.569 45
	180.63	S_A	0.001 00	0.699 71	0.349 34	0.499 26	0.569 46
	< 180.6	N_R					

TABLE IV. Effect of pressure on the transition properties for the system in which $r=4$, $f=8$, and $E_b/k=250$ K.

Pv_0/k (K)	Transition	T (K)	$\Delta\rho/\rho_{\text{mop}}$ (%)	$\Delta S_c/(Nk)$
43.00	N-I	180.72	4.0221	0.682 66
43.50	S_A-I	181.39	4.4692	0.745 01
	N_R-S_A	180.6	$0\leftarrow$	$0\leftarrow$

Effect of pressure

Tables I–IV illustrate some of the effects of the pressure on the stabilities of the S_A, N, and I phases. Decreasing P favors the N phase, while increasing P favors the S_A phase over the high-T N phase for the range of pressures treated in this paper. As expected, T for a given transition increases as P increases, a trend seen experimentally (see, for example, Refs. 2, 17, 34, and 35). Higher P leads to larger ρ which favors the more ordered phases at higher T. This increased molecular order at higher T is reflected in the values of λ, η, and τ in Tables I and III.

As seen in Tables II and IV, decreasing P increases the relative density and relative entropy changes at the N-I transition, as expected.[2] These changes at the S_A-I transition in Table IV are the same order of magnitude as the changes at the N-I transition and are about an order of magnitude larger than those at the S_A-N transition in Table II, results consistent with some experimental data.[22,32]

Effect of tail-chain flexibility

Tables I, II, V, and VI illustrate some of the effects of tail-chain flexibility (as determined by the tail bond-bending energy E_b) on the relative stabilities of the S_A, N, and I phases. Decreasing E_b/k makes the tails more flexible and thus makes the packing characteristics of the tails increasingly different from those of the rigid core, thereby favoring the segregated packing of the S_A phase over the unsegregated packing of the N phase. (These changes in E_b/k can be seen in the changes in the *intra*molecular tail orientational-order parameter ν in the tables.)

Decreasing E_b/k also decreases the lower limit of the temperature range over which the I phase is the stable phase; making the tails more flexible makes it more difficult to orientationally order the cores, either in an S_A phase or in an N phase. For an orientationally-ordered phase to be *the* stable phase in *some* temperature ranges, the ordered phase must be the S_A phase with $\lambda=1$, as seen in Table V. With $\lambda=1$, the segregated packing is at a maximum, thus minimizing the opportunities of the rather flexible tails to disrupt the orientational order of the cores.

For $E_b/k=100$ K in Table V, the core orientational order parameter η in the S_A phase first increases with decreasing T (as might be expected), goes through a maximum, and then decreases somewhat slowly with decreasing T; this maximum in η would appear to occur at some T around that at which $\lambda\rightarrow 1$ as *T increases.* At a constant value of λ (here $\lambda=1$), η can be expected to increase as T decreases. Then, as λ decreases, η can be expected to decrease, since η and λ are coupled. The behavior of the *inter*molecular tail orientational order parameter τ in the S_A phase in Table V mimics that of η. However, due to the competing effect of η and ν, the maximum in τ appears to occur at a lower T than that for the maximum in η.

The density ρ in the S_A phase for $E_b/k=100$ K in Table V increases as η increases and decreases as η decreases; the molecules can pack more densely if their cores are more orientationally ordered.

Effect of tail length

Tables I, II, VII, and VIII illustrate some of the effects of the tail-chain length (as measured by the number f of

TABLE V. Effect of tail bond-bending energy on the thermodynamic and molecular ordering properties for the system in which $r=4$, $f=8$, and $Pv_0/k=43.25$ K.

E_b/k (K)	T (K)	Stable phase	λ	η	τ	ν	ρ
100	>112.16	I					
	112.16	I				0.324 16	0.650 00
		S_A	1.000 00	0.722 93	0.234 35	0.324 16	0.672 70
	100.00	S_A	1.000 00	0.904 80	0.329 50	0.364 18	0.716 63
	86.00[a]	S_A	1.000 00	0.967 09	0.409 01	0.422 93	0.760 64
	83.09	S_A	0.600 00	0.941 57	0.411 77	0.437 33	0.757 58
	82.11	S_A	0.300 00	0.929 62	0.411 27	0.442 40	0.756 92
	81.83	S_A	0.100 00	0.925 98	0.410 97	0.443 82	0.756 77
	81.80	S_A	0.001 00	0.925 53	0.410 93	0.443 99	0.756 75
	<81.80	N_R					
400	>249.58	I					
	249.58	I				0.569 37	0.474 26
		N		0.696 42	0.396 52	0.569 37	0.501 75
	<249.58	N					

[a] As T increases, $\lambda\rightarrow 1$ at $T=86.00$ K.

TABLE VI. Effect of tail bond-bending energy on the transition properties for the system in which $r=4$, $f=8$, and $Pv_0/k=43.25$ K.

E_b/k (K)	Transition	T (K)	$\Delta\rho/\rho_{\text{mop}}$ (%)	$\Delta S_c/(Nk)$
100	S_A-I	112.16	3.3741	0.420 67
	N_R-S_A	81.80	$0\leftarrow$	$0\leftarrow$
400	N-I	249.58	5.4792	0.739 68

semiflexible segments) on the relative stabilities of the S_A, N, and I phases. As f increases, the N-I transition temperature $T_{N\text{-}I}$ increases for larger E_b/k (as seen in Tables I and VII) and decreases for smaller E_b/k.[2] Here, for $E_b/k=250$ K at $Pv_0/k=43.25$ K, the semiflexible tails have sufficient rigidity that the effect of increasing the tail length is to enhance the orientational ability of the cores by increasing the overall length-to-breadth ratio of the molecule, thus making the cores orient at increasingly higher T, either in the N or the S_A phase. As f increases, the S_A solutions exist at higher T. In fact, the S_A solutions for $f=9$ in Table VII are found at T greater than $T_{N\text{-}I}$, and $\lambda\to 0$ at a T just higher than $T_{N\text{-}I}$. However, the S_A solutions for $f=9$ are metastable with respect to the I phase. These results can be understood by considering the following.

As f increases, the segregated packing of the S_A phase becomes increasingly important, at increasingly higher T, in minimizing the opportunities of the semiflexible tails to disrupt the orientational order of the cores. The tails are sufficiently rigid to shift the T ranges of both the S_A solutions and the N solutions to higher T as f increases, but the tails are still flexible enough to shift the T range of the S_A solutions to higher T more rapidly than the T range of the N phase; hence, for $f=9$ in the S_A phase, $\lambda\to 0$ at a T just greater than $T_{N\text{-}I}$. The S_A solutions are metastable with respect to the I phase because at the higher T at which the S_A solutions now exist, the densities are sufficiently small that the molecules do not need to orient at all in order to achieve the state of lowest G_c.

No S_A solutions were found for $f<4$ with $r=4$ and with varying values of E_b/k and Pv_0/k. Preliminary calculations for the system in which $r=4$, $f=4$, $E_b/k=250$ K, and $Pv_0/k=43.25$ K indicate that there may be a stable S_A phase at *very* low T (around 30 K); at higher T, no S_A solutions appear to exist. That the existence of S_A solutions appears to require an f greater than some minimum value agrees with experiment.[22]

In Tables I and VII, the size of the T range over which the S_A phase is *stable* for a given range of λ (where $\lambda<1$) decreases as f decreases. Also, for $\lambda<1$, the size of the T range over which S_A *solutions* exist—whether or not these solutions correspond to the most stable state of the system at a given P and T—decreases as f decreases. These results are consistent with experiment. Because the chains are so short, in order for an S_A phase to exist at all in some T ranges for shorter f, there must be perfect S_A order (i.e., $\lambda=1$).

In Tables V and VII, the regions in which $\lambda=1$ as T increases have not yet been seen experimentally. Later in this series of papers[23] on the S_A phase, both attractive and soft repulsive segmental (site-site) intermolecular interactions are also included in the models; then, if an N_R phase exists at all, λ goes through a maximum at values significantly smaller than unity as T decreases. With these more realistic intermolecular potentials, the molecules interact with each other at distances larger than the "hard-repulsion" (steric) separation distance between segment centers; thus, the densities of the systems are smaller than those in the present model with only hard repulsions, and the S_A phase is less favored over the N phase. With the more realistic intermolecular potentials, the size of the T range over which the S_A phase is the stable phase increases as f increases.

In Table VII the maxima in η, τ, and ρ in the S_A phase for $f=7$ and $E_b/k=250$ K are similar to those in Table

TABLE VII. Effect of tail-chain length on the thermodynamic and molecular ordering properties for the system in which $r=4$, $E_b/k=250$ K, and $Pv_0/k=43.25$ K.

f	T (K)	Stable phase	λ	η	τ	ν	ρ
7	>179.93	I					
	179.93	I				0.501 05	0.539 93
		S_A	1.000 00	0.794 78	0.398 23	0.501 05	0.578 01
	174.00	S_A	1.000 00	0.861 19	0.444 96	0.516 69	0.595 27
	168.29[a]	S_A	1.000 00	0.900 05	0.479 28	0.532 50	0.610 09
	165.50	S_A	0.600 00	0.865 25	0.467 71	0.540 55	0.605 45
	164.45	S_A	0.300 00	0.850 36	0.462 27	0.543 62	0.603 95
	164.15	S_A	0.100 00	0.845 96	0.460 62	0.544 49	0.603 56
	164.11	S_A	0.001 00	0.845 41	0.460 41	0.544 60	0.603 51
	<164.1	N_R					
9	>188.57	I					
	188.57	I				0.479 61	0.538 06
		N		0.665 26	0.319 07	0.479 61	0.558 64
	<188.57	N					

[a] As T increases, $\lambda\to 1$ at $T=168.29$ K.

TABLE VIII. Effect of tail-chain length on the transition properties for the system in which $r=4$, $E_b/k=250$ K, and $Pv_0/k=43.25$ K.

f	Transition	T (K)	$\Delta\rho/\rho_{\mathrm{mop}}$ (%)	$\Delta S_c/(Nk)$
7	S_A-I	179.93	6.5890	0.745 99
	N_R-S_A	164.1	0←	0←
9	N-I	188.57	3.6829	0.681 06

V for $f=8$ and $E_b/k=100$ K and are generated by the same conditions in λ.

General concluding remarks

The present model for smectic-*A* and reentrant-nematic phases is unique in that the molecules are composed of rigid cores with *semi*flexible tail chains and have only site-site (segmental) hard repulsive intermolecular interactions. This latter feature of the model allows us to concentrate exclusively on differences between the steric (hard-repulsion) packing of the rigid cores and of the semi-flexible tail chains.

The results for the smectic-*A* and reentrant-nematic phases show, for the first time, that these packing differences (and changes in these differences) are sufficient to produce and stabilize both of these phases in different ranges of temperature and pressure. This observation explains why the necessary condition, with very few exceptions, for molecules to form smectic-*A* liquid crystals in real systems is the presence of semiflexible tail chains of significant length and why the smectic-*A* phase (in fact, any smectic phase) disappears as the length of the tail chain is shortened.

As with the ordinary (high-temperature) nematic phase,[2] dipolar interactions are not necessary in this steric packing model to produce smectic-*A* and reentrant-nematic phases, but (as will be seen in future papers[23] of this series) do affect the ranges of temperature and pressure for which such phases are stable.

As in any model with only hard repulsive interactions,[2] pressures larger than atmospheric are required to produce condensed phases. Hence, the important aspect of the numerical results here is the reproduction, qualitatively and semiquantitatively, of experimental *trends*. The temperatures in this paper tend to be low compared with experiment,[2,17–19,22,32] but the important feature in this model is not so much the absolute magnitude of the temperature, but rather the *ratio* of the tail bond-bending energy E_b to the temperature; the values used here for this ratio agree well with experiment.[2]

The idea that the packing differences (and changes in these differences) between rigid parts and semiflexible parts of molecules give rise to smectic-*A* and reentrant-nematic phases can also be used to explain these phases in disklike liquid crystals, in which the rigid rodlike core of a molecule has been replaced by a rigid disk.[36]

Observing the way the packing differences give rise to the smectic-*A* phase in a pure component, we can make some comments about how solute molecules of different shapes will pack when introduced into a smectic-*A* solvent and thus affect the stability of the smectic-*A* phase of the solvent.

In particular, the more flexible solutes would be expected to concentrate with the semiflexible tail chains of the solvent molecules in the smectic-*A* phase, and the more rigid, rodlike solutes would be expected to concentrate with the solvent rigid cores. The more globular, quasispherical solutes would be expected to pack with the solvent tail chains in the smectic-*A* phase in order to minimize the disruption of the orientational ordering of the cores.

On a volume-fraction basis, quasispherical solutes are more effective than semiflexible chain solutes in disrupting the orientational order of a nematic solvent,[30] because the chains tend to align somewhat with the solvent cores and tails. In the smectic-*A* phase, one might expect the same relative disrupting abilities of the quasispherical solutes and the chain solutes, with both solutes tending to concentrate with the solvent tail chains. However, if the solute chain is long enough, it could overlap into the regions where the solvent rigid cores are concentrated and thus could be more effective, on a volume-fraction basis, than a quasispherical solute in disrupting the orientational order of the solvent cores of the smectic-*A* phase as well as the smectic-*A* order (i.e., the segregation of cores with cores and tails with tails).

The model of this paper is presently being extended to treat binary mixtures of solutes of various shapes in smectic-*A* solvents in order to test directly the above observations, which do seem to be consistent with experimental data for binary mixtures of solutes of various shapes in smectic-*A* solvents.[37]

These observations also suggest that when solutes are used as probes[38,39] of the orientational order in a smectic-*A* phase, the structure of a solute molecule will determine with which parts of the solvent molecules the solute molecule will tend to pack and thus for which part of a solvent molecule the order is actually being probed.

ACKNOWLEDGMENTS

P. E. Cladis, J. D. Litster, J. W. Goodby, and R. Pindak are acknowledged for very helpful discussions about the experimental aspects of smectic and reentrant-nematic phases. This research was supported by the U. S. Department of Energy. (Some of the early work on the model in this paper was performed while the author was on the staff of Oak Ridge National Laboratory and was supported by the Office of Basic Energy Sciences, U. S. Department of Energy.)

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