

Steric molecular theory for multiple smectic- A phases

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Molecular-lattice-theory results reveal that the steric (hard-repulsive) packing of rigid cores and partially flexible tails can explain the relative stabilities of the smectic- A_1 , smectic- A_d , and higher-temperature and lower-temperature nematic (including reentrant-nematic) liquid-crystalline phases, and the isotropic liquid phase. These phases and transitions between them are presented as a function of temperature, pressure, tail-chain length and flexibility, and orientational and positional order of the molecules for different systems. Critical exponents calculated at the smectic- A_d to nematic transitions are consistent with an identification of the fraction of one-dimensional positional alignment (i.e., the fraction of segregated packing of cores with cores and thus of tails with tails) of the molecules in the smectic- A_d phase as an order parameter.

INTRODUCTION

The partial orientational alignment of the long axes of molecules parallel to a preferred axis (and also, in some cases, the partial positional alignment of the centers of mass of molecules) to form liquid-crystalline phases is very common in nature and therefore is of considerable basic interest to theoreticians and experimentalists, as well as of significant practical importance to engineers. The simplest (least-ordered) phase with *both* partial orientational and partial positional ordering of the molecules is the smectic- A (S_A) phase. Depending on the relation between the molecule length d_L and the S_A layer thickness L , there are distinct types of S_A phases, with real phase transitions between the different types.¹

In this paper we shall be concerned with two types of S_A phases, the smectic- A_1 (S_{A_1}) phase and the smectic- A_d (S_{A_d}) phase. These phases are physically defined¹ by the following relations between L and d_L : $L = d_L$ in the S_{A_1} phase and $d_L < L < 2d_L$ in the S_{A_d} phase.

The major purpose of this paper is to show, for the first time, that different S_A phases—in particular, distinct S_{A_1} and S_{A_d} phases—can exist in systems of molecules that are composed of rigid, rodlike cores and pendant, partially flexible tail chains and that interact through only hard-repulsive (steric, or infinitely large repulsive) site-site (segmental) forces. It is not necessary to invoke dipolar forces (or even attractive forces) to have these phases. This paper also shows, for the first time, the relative stabilities of the S_{A_1} , S_{A_d} , high-temperature nematic (N), and low-temperature N [including reentrant-nematic (N_R)] liquid-crystalline phases and the isotropic (I) liquid phase as a function of temperature, pressure, tail-chain extended length, tail-chain flexibility, orientational ordering, and positional ordering in these simple molecular systems.

In the nematic phases there is no long-range positional alignment of the molecules, but there is partial orientational alignment of the molecules. The N_R phase is a stable N phase that reenters (reappears) at temperatures

lower than those at which the more-ordered S_A (or other smectic) phases appear.

This paper shows, for the first time, critical exponents for some molecular properties at the S_{A_d} - N transitions in these simple molecular systems. The nature of the S_{A_1} - S_{A_d} transition in these molecular systems is also presented.

A theory for these simple molecular systems provides a base or reference theory to which other molecular features [such as site-site (segmental) intermolecular forces, including (1) attractions (arising from London dispersion forces), (2) soft repulsions (i.e., finite-sized repulsions), and (3) dipolar forces (including dipole-dipole forces and dipole-induced dipole forces)] can be added. In fact, theories with these additional molecular features have been studied² by this author and are in the process of being written up for publication. This stepwise theoretical approach provides a method for determining on an individual basis which molecular features are sufficient and/or necessary (and/or helpful) for the existence of S_{A_1} , S_{A_d} , and N_R phases and also the relative importance, one with respect to the other, of these features in affecting the relative stabilities of the various phases.

The motivation for starting with these simple systems of molecules that are composed of cores and partially flexible tails and that interact with only segmental hard repulsions is the experimental observation that almost all systems that form S_A and N_R phases [in fact, that form *any* kind of smectic (i.e., layered) liquid-crystalline phase] are composed of molecules each of which has one or more pendant partially flexible tail chains: as the tail chain is shortened, the smectic phases disappear.³ While there are a few exceptions⁴ to this observation, our purpose here is to focus on what the tail chains are doing in the S_{A_1} , S_{A_d} , and N_R phases in the much more commonly observed systems. While many of these molecular systems with tails also have dipolar forces, our purpose in this paper is to focus on and isolate the effects of steric packing of cores and partially flexible tails in stabilizing S_{A_1} , S_{A_d} , and N_R phases.

THEORY

We use here a mean-field-like simple cubic lattice theory^{5,6} derived by this author for a system of molecules where each molecule is composed of a rigid, rodlike core and one or two pendant, partially flexible (semiflexible) tail chains. Each molecule has a total of m cubic segments occupying m contiguous lattice sites; there are r rigid core segments, f semiflexible tail segments, $r-1$ rigid core bonds, and f semiflexible tail bonds. By semiflexible we mean that it costs an energy E_b to bend a tail bond out of the direction of the long molecular axis of the core. To mimic alkyl chains, each tail bond has three choices of direction, two of which each cost an energy E_b . In this theory the average fraction $2u$ of bent tail bonds depends only on E_b and the temperature T and is set by a Boltzmann distribution.⁵

The molecules interact only through steric (hard-repulsive), site-site (segmental) intermolecular interactions. By hard-repulsive we mean that it costs an infinitely large energy to place two molecular segments on the same lattice site.

The general configurational partition function for this theory is derived and discussed in detail elsewhere.^{5,6} To summarize, the partition function is derived for given orientational and positional orderings of the molecules at given pressures and temperatures by counting (via approximate combinatorial lattice statistics) the number of ways that the molecules in the system can be laid, segment by segment, in a lattice of given volume in a manner such that two molecular segments do not occupy the same lattice site (hence, hard repulsions), and then taking the thermodynamic limit.

More specifically, the configurational partition function is a function of the following molecular and thermodynamic variables: P , pressure; T , absolute temperature; ρ , average density of the system (average fraction of lattice sites occupied by molecular segments; $0 < \rho \leq 1$); v_0 , volume of one lattice site (thus, hard-repulsive volume of one molecular segment); m , total number of segments in a molecule; r , number of core segments in a molecule; f , number of tail segments in a molecule; E_b , tail-bond bending energy, as described earlier; η , average orientational order of the molecular cores [given by $\eta = \langle (3 \cos^2 \theta - 1) \rangle / 2$, where θ is the angle between the core long axis and the preferred axis of orientation for the cores; $0 \leq \eta \leq 1$]; and λ , average fraction of one-dimensional (1D) positional alignment of molecules whose cores are oriented parallel to the preferred axis for core orientation [λ in this theory is a real number defined^{5,6} in terms of the literal physical packing of the core and tail parts of the oriented molecules. More specifically, λ is actually the average fraction of the length of an oriented molecule that overlaps (positionally aligns with)—in excess of overlaps from random positional packing—the lengths of oriented neighboring molecules, such that cores tend to pack with cores and tails tend to pack with tails for oriented molecules. This λ is used in the actual molecular packing statistics^{5,6} for a S_A layer and in the resulting thermodynamic equations of this theory; $0 \leq \lambda \leq 1$].

Four pertinent thermodynamic equations⁶ resulting from this partition function are given below to illustrate how the molecular structure is coupled explicitly to the molecular ordering and thermodynamic properties of the system:

$$Pv_0/kT = \sum_{l=R,F} [(1-C_l)(\ln Q_{l1} + 2 \ln Q_{l2} - \ln C_l) C_{l6}/2pm], \quad (1)$$

$$\left[\frac{\partial G(NkT)^{-1}}{\partial \eta} \right]_{P,T,\lambda} = - \left[\left[\sum_{l=R,F} [-(C_3 + q\lambda C_4) \ln Q_{l1} + (C_3 + 2q\lambda C_5) \ln Q_{l2} + q\lambda(r-f) \ln C_1] \right] + 2 \ln[(1-\eta)/(1+2\eta)] \right] / 3 = 0, \quad (2)$$

$$\left[\frac{\partial G(NkT)^{-1}}{\partial \lambda} \right]_{P,T,\eta} = (1+2\eta) \left[\sum_{l=R,F} [qC_4 \ln Q_{l1} - 2qC_5 \ln Q_{l2} - q(r-f) \ln C_1] \right] / 6 = 0, \quad (3)$$

$$\mu/kT = \left[\sum_{l=R,F} \{[(1-Q_{l1}) \ln Q_{l1} + 2(1-Q_{l2}) \ln Q_{l2} - (1-C_l) \ln C_l] C_{l6}/2p\} \right] + C_2, \quad (4)$$

where

$$Q_{l1} = 1 - (\rho/3C_{l6}) \{ (1+2\eta)[(r-1) + q\lambda C_4] + (1+2\eta\nu)f \}, \quad (5)$$

$$Q_{l2} = 1 - (\rho/3C_{l6}) \{ (1-\eta)(r-1) + (1-\eta\nu)f - q(1+2\eta)\lambda C_5 \}, \quad (6)$$

$$C_1 = 1 - \rho, \quad (7)$$

$$C_2 = \{ [(1+2\eta) \ln(1+2\eta) + 2(1-\eta) \ln(1-\eta)] / 3 \} + \left[\sum_{l=R,F} [\ln(\rho/3C_{l6})] / 2 \right], \quad (8)$$

$$C_3 = r - 1 + \nu f, \quad C_4 = r - [(1+2\nu)f/3], \quad (9)$$

$$C_5 = (1-\nu)f/3, \quad C_{l6} = m + q[(1+2\eta)\lambda(r-f)/3], \quad (10)$$

$$m = r + f, \quad (11)$$

N is the number of molecules in the system, k is the Boltzmann constant, μ and G are the configurational chemical potential and configurational Gibbs free energy, respectively, of the system, ν is the average tail intramolecular orientational order, where

$$\nu = \langle (3 \cos^2 \psi - 1) \rangle / 2 = 1 - 3[\Lambda / (1 + 2\Lambda)], \quad (12)$$

where

$$\Lambda = \exp(-E_b/kT), \quad (13)$$

and ψ is the angle between a given tail bond and the core of the molecule to which the tail bond is attached.

The 1D positional alignment of oriented molecules is the basis of S_A layers. This actual positional alignment (i.e., segregated packing) of cores with cores (and thus, of tails with tails) for oriented molecules in this theory results in a core-rich region (labeled R) and (a) tail-rich region(s) (labeled F) in each layer. If $l=R$ in the above equations, then $q=+1$, if $l=F$, then $q=-1$. When $\lambda=0$, these regions have the same segmental composition and there is no layering. A S_A phase of some kind exists for any value of λ for which $0 < \lambda \leq 1$.

Within the physical constraints $0 < \rho \leq 1$, $0 \leq \eta \leq 1$, and $0 \leq \lambda \leq 1$, Eqs. (1)–(3) are solved simultaneously (via numerical computer iteration) to obtain the numerical values of ρ , η , and λ in the various phases of the system at given P and T . At a transition between two phases 1 and 2, $\mu_1 = \mu_2$.

By the physical definitions of the various phases, $\eta=0$ in the I phase, and $0 < \eta \leq 1$ in the N and S_A phases. $\lambda=0$ in the I and N phases.

Physically, the only way to have a S_{A_1} phase (i.e., to have $L=d_L$; recall the definitions in the Introduction) is to have total 1D positional alignment of the molecules (i.e., to have $\lambda=1$); therefore, $\lambda=1$ in the S_{A_1} phase. The only way to have a S_{A_d} phase (i.e., to have $d_L < L < 2d_L$) is to have partial, but not total, 1D positional alignment of the molecules (i.e., to have $0 < \lambda < 1$); therefore, $0 < \lambda < 1$ in the S_{A_d} phase. (See Fig. 7 in Appendix A for schematic diagrams of the S_{A_1} and S_{A_d} phases.)

The exact mathematical relation between λ and L in this theory is determined in the following manner. Since λ is the average fraction of positional alignment of molecules, $1-\lambda$ is the average fraction of positional disalignment and hence the average fraction of the length of a given molecule that is out of register with its neighbors in the S_A plane. Therefore, the layer thickness L in this theory is given⁶ by

$$L = d_L + (1-\lambda)d_L = (2-\lambda)d_L, \quad (14)$$

where the molecular length d_L is given by

$$d_L = r + f[(1+2\nu)/3]. \quad (15)$$

Because of the mean-field-like approximations, this steric theory⁵ here does not distinguish between the cases of a molecule with one tail and a molecule with two tails. Consequently, there is no mechanism in this theory for identifying the bilayer smectic- A_2 (S_{A_2}) phase¹ (in which $L=2d_L$) formed by one-tail molecules. The addition of

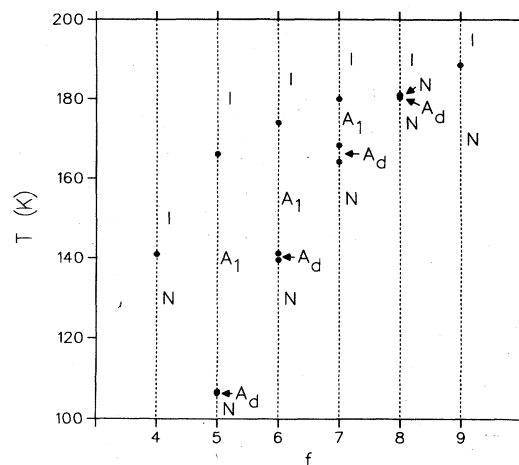


FIG. 1. Phase transition temperatures T (indicated by dots) as a function of tail extended length f for the system in which $r=4$, $Pv_0/k=43.25$ K, and $E_b/k=250$ K. The phase names are abbreviated in the following manner: isotropic (I), nematic (N), smectic- A_1 (A_1), and smectic- A_d (A_d). The dotted lines are drawn to aid the eye in following lines of constant value on the abscissa.

other segmental intermolecular forces (such as attractions, etc.) to this theory does result² in such a distinction in tail number, as will be seen in papers presently being prepared by this author for publication.

RESULTS AND DISCUSSION

Some representative results calculated from the lattice theory summarized above are presented in Figs. 1–6. These results are shown to illustrate *general* patterns and trends. Numerical results from this theory are somewhat time consuming to obtain since they are produced by somewhat tedious computer iterations that simultaneously solve Eqs. (1)–(3). Therefore, fine details of the general

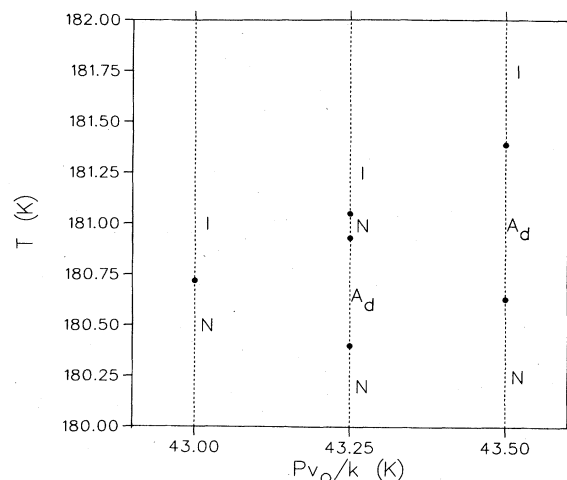


FIG. 2. Phase transition temperatures as a function of small changes in pressure (specifically Pv_0/k) for the system in which $r=4$, $f=8$, and $E_b/k=250$ K. The symbols and dotted lines are defined as in Fig. 1.

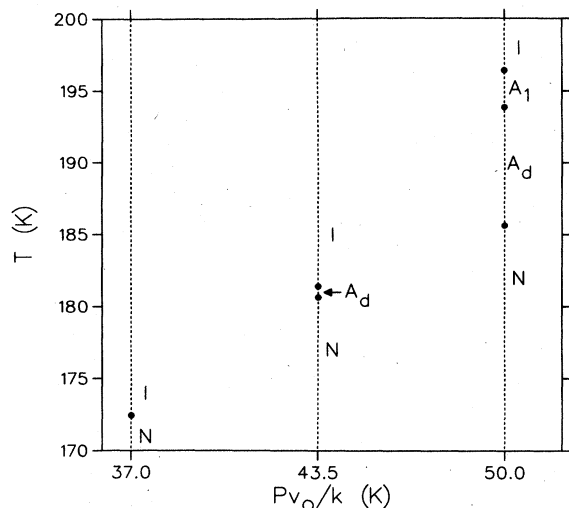


FIG. 3. Phase transition temperatures as a function of larger changes in pressure (specifically P_{v_0}/k) for the system in which $r=4$, $f=8$, and $E_b/k=250$ K. The symbols and dotted lines are defined as in Fig. 1.

patterns and trends presented in Figs. 1–6 are properly left to be generated for later, more exhaustive papers.

As outlined in the Theory section, the partition function (and thus the resulting thermodynamic equations, and in turn the resulting thermodynamic properties and molecular orderings) is a function of certain molecular and thermodynamic variables. It should be noted that these variables are *not* treated as *ad hoc*, arbitrarily adjustable parameters, but rather (if used as input to the equations of the theory) are taken from experimental data or (if explicitly calculated by the theoretical equations) are compared with experiment. A discussion of specific numerical values for these variables used in this paper fol-

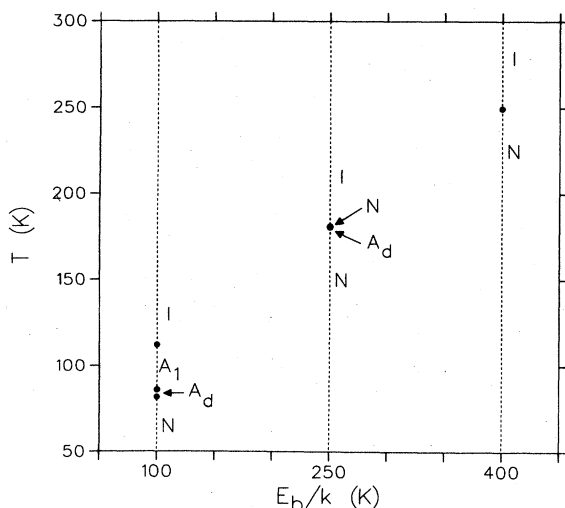


FIG. 4. Phase transition temperatures as a function of reduced tail bond-bending energy E_b/k for the system in which $r=4$, $f=8$, and $P_{v_0}/k=43.25$ K. The symbols and dotted lines are defined as in Fig. 1.

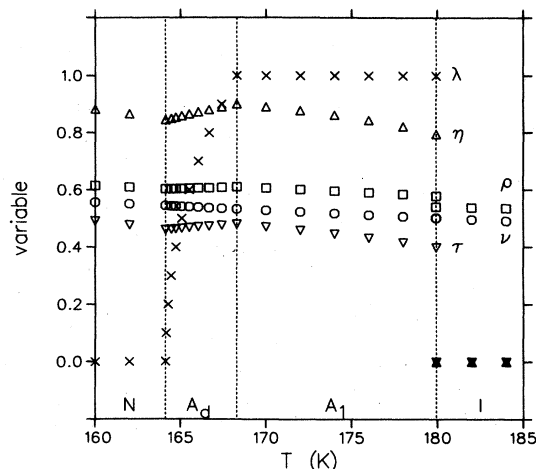


FIG. 5. Molecular ordering and thermodynamic variables λ , η , τ , ν , and ρ as a function of temperature in different phases for the system in which $r=4$, $f=7$, $P_{v_0}/k=43.25$ K, and $E_b/k=250$ K. The dotted lines denote phase boundaries at constant T . The phase-name abbreviations are defined as in Fig. 1.

lows.

The number r of core segments used in this paper is 4. The value $r=4$ is reasonable compared with length-to-breadth ratios for cores in real liquid crystals;^{7–9} furthermore, a stable N phase is not observed for rigid rods having an r less than about 3.6 in the simple cubic lattice model with only hard repulsions.¹⁰

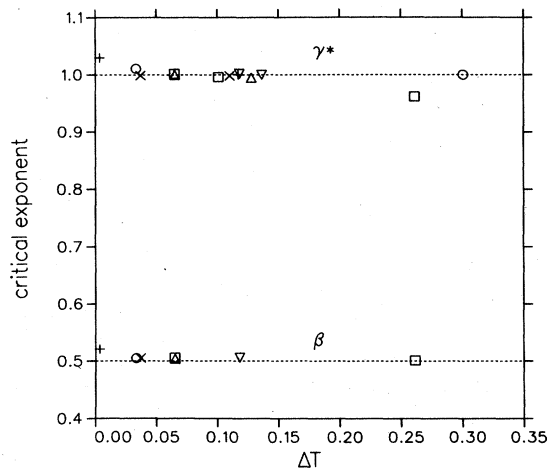


FIG. 6. Critical exponents β and γ^* at the S_{A_d} - N transitions as a function of ΔT for different systems, indicated by the following symbols (P_{v_0}/k and E_b/k are in K): (+) $r=4$, $f=5$, $P_{v_0}/k=43.25$, $E_b/k=250$; (×) $r=4$, $f=7$, $P_{v_0}/k=43.25$, $E_b/k=250$; (□) $r=4$, $f=8$, $P_{v_0}/k=43.25$, $E_b/k=250$; (Δ) $r=4$, $f=8$, $P_{v_0}/k=43.5$, $E_b/k=250$; (∇) $r=4$, $f=8$, $P_{v_0}/k=300$, $E_b/k=250$; (○) $r=4$, $f=8$, $P_{v_0}/k=43.25$, $E_b/k=100$. The dotted lines are drawn to aid the eye in following lines of $\beta=0.5$ and $\gamma^*=1$.

In this paper the number f of tail segments varies from 4 to 9. Using simple space-filling models, one can argue that each cubic tail segment in this lattice theory contains one to two methylene ($-\text{CH}_2-$) units. This range in f values and the corresponding range in methylene units are in good agreement with tail extended lengths in experimentally observed systems that have S_A and N_R phases.

Most calculations in this paper were performed for the reduced tail bond-bending energy $E_b/k = 250$ K, the approximate lower limit (as estimated from experimental data) for the energy to make a *trans-gauche* bend in a hydrocarbon chain.^{7,11} (The approximate upper limit corresponds to $E_b/k = 400$ K.)

In this paper results are reported for values of the more general ratio Pv_0/k , rather than for the less general quantity P , the pressure. To convert the Pv_0/k values in this paper to P values, an appropriate value for the hard-repulsive volume v_0 was calculated to be 2.98×10^{-23} cm³ via the procedure outlined in Appendix B. Most calculations are reported for $Pv_0/k = 43.25$ K, which corresponds to $P = 198$ atm, using this value of v_0 .

As is well known,^{6,7} condensed phases can only exist at higher pressures and/or lower temperatures in theories in which the molecules interact only through hard-repulsive forces than in theories in which molecules also interact through attractive forces. Though the temperature ranges over which some phases are stable in the following figures are sometimes somewhat small, these T ranges are both significant and real.

Figures 1–4 illustrate the relative stabilities of the S_{A_1} , S_{A_d} , N , and I phases and the temperatures of the transitions between pairs of these phases as a function of tail-chain extended length, of small pressure changes, of larger pressure changes, and of tail-chain flexibility, respectively. Figure 5 shows the average values of the density, the 1D positional order of the molecules, the orientational order of the cores of the molecules, the *intermolecular* orientational order of the tails of the molecules, and the *intramolecular* orientational order of the tails of the molecules calculated in the stable phases in a representative system as a function of temperature. Figure 6 shows critical exponents β and γ^* calculated for the 1D positional order of the molecules and the density, respectively, for the S_{A_d} - N transitions for molecular systems with different tail-chain extended lengths, pressures, and tail-chain flexibilities.

In the following figures these transitions are second order: S_{A_d} - N (except as noted) and S_{A_1} - S_{A_d} . These transitions are weakly first order: N - I , S_{A_d} - I , S_{A_1} - I , S_{A_1} - N . In accord with experiment,^{3,12} the relative density and relative entropy changes at the S_A - I transitions are about the same order of magnitude as the changes at the N - I transitions and are about an order of magnitude larger than those at the S_{A_1} - N transition.

Effect of tail-chain extended length

The results in Fig. 1 for tail-chain extended length $f = 8$ for a representative molecular system can be understood as follows. At higher temperature T , the system

volume V is large enough that the molecules can pack randomly, and thus the drive for maximum entropy leads to the existence of a stable I phase. As T is lowered, V decreases, the molecules must order partially to fit in the volume, and there is thus a transition to a stable N phase.

As T decreases further, V decreases further, and there is a very weakly first-order transition to a stable S_A phase (here, the S_{A_d} phase). In the S_A range the tails are flexible enough and V is small enough that the molecules will pack with lowest G if, for oriented molecules, cores *tend* to pack with other cores and tails pack with other tails. The semiflexible tail chains bend and twist well around each other, but do not pack as well with the rigid cores.

As T decreases even further, there is a transition from the S_{A_d} phase to a low-temperature nematic phase (here, a N_R phase). As T decreases, the tails become less flexible and more closely resemble a rigid extension of the rigid core. The difference in packing cores and tails thus decreases; the need for segregated packing of cores with cores and tails with tails (as in a S_A phase) is diminished and is now overcome by the entropy of unsegregated packing, thereby leading to the reappearance of a stable N phase. The transition is precipitated by *subtle* changes in the flexibility of the tails, as evidenced by the fact that while the tail chains are *less* flexible at the transition, they are still somewhat flexible and are certainly not completely rigid. (See, for example, the ν values in Fig. 5.)

The results for $f = 5$ – 7 are somewhat similar, except that the higher-temperature N phase has been replaced by a S_{A_1} phase. For $f = 5$ – 7 , the differences in packing cores and tails is large enough so as to force total positional alignment of oriented molecules (i.e., $\lambda = 1$, and thus the stable phase is S_{A_1} , as opposed to a S_{A_d} or N phase). As T is lowered, the tails become less flexible, and the differences in packing cores and tails decrease—at first just enough such that some, but not total, positional alignment is needed (hence, the stable S_{A_d} phase) and finally enough such that no positional alignment is needed (hence, the stable low-temperature N phase).

No stable S_A phases [that satisfy Eqs. (1)–(3)] were found for $f \leq 4$; this result is consistent with the observation³ (see the Introduction) that smectic phases disappear as the tail chain is shortened in practically all systems that have been studied experimentally thus far. Whether one tail segment in this theory is assigned one or two methylene units, the smallest f in Fig. 1 for which a S_A phase exists is in good agreement with the minimum number of carbon atoms needed in the tail chain(s) of many experimental systems^{3,13–15} to have S_A behavior. When the number f of tail segments becomes much smaller than the number r of core segments, the packing of the tail segments seems to act as a minor perturbation to the packing of the cores—so minor that the segregated packing of cores with cores and tails with tails in a S_A phase is no longer necessary, and the drive to maximize entropy favors the (more-disordered) N phase over a S_A phase.

No stable S_A phases [that satisfy Eqs. (1)–(3)] were found for $f \geq 9$ for $Pv_0/k = 43.25$ K. When f becomes much larger than r , the packing of the cores seems to act as a minor perturbation to the packing of the tails—so

minor that the segregated packing of cores with cores and tails with tails in a S_A phase is no longer necessary, and the drive to maximize entropy favors the N phase over a S_A phase.

For $f=5-7$ in Fig. 1, the size of the combined temperature range of the S_A phases decreases with increasing number of tail segments, a trend that has been observed experimentally¹³⁻¹⁵ (although the opposite trend has been seen in experiment more frequently to date¹³). For $f=5-7$, the size of the temperature range of the S_{A_d} phase increases with increasing f , a trend that has also been observed experimentally.¹

Effect of pressure

As seen in Figs. 2 and 3 for a representative system, the S_A phases become stable as the pressure P is increased at constant lattice site volume v_0 , as expected. Also as expected, the S_{A_d} phase (which has less positional alignment) becomes stable at lower P than the S_{A_1} phase (which has more positional alignment). Larger P leads to larger ρ , which favors the more ordered phases.

Effect of tail-chain flexibility

As seen in Fig. 4 for a representative system, the S_A phases become stable as the tails become more flexible (i.e., as the tail bond-bending energy E_b decreases), as expected. Making the tails more flexible increases the packing differences between the cores and the tails, thus favoring the segregated packing of the S_A phases. As expected, the S_{A_d} phase (with less segregated packing) is stable at larger E_b than is the S_{A_1} phase (with more segregated packing).

As discussed earlier, the ranges of $E_b/k=250-400$ K are considered to be especially appropriate for hydrocarbon chains. The smaller E_b/k values in Fig. 4 might possibly be realized experimentally in hydrosilicon chains.

Values of molecular ordering and thermodynamic variables

The average density ρ , 1D positional order λ , core orientational order η , and tail intramolecular orientational order ν were defined in the Theory section. The tail intermolecular orientational order τ is the tail analog of η and is given⁶ by $\tau=\eta\nu$. For each of the λ , η , τ , and ν variables, unity denotes complete order, and zero denotes no order. η (and thus τ) and λ are zero in the I phase, and λ is zero in the N phase. λ is unity in the S_{A_1} phase.

As seen by the values of η and τ in Fig. 5 for a representative system, neither the cores nor the tails have complete orientational order, even in the S_A phases. While the tails become less flexible (i.e., more rigid) as T decreases, the tail intramolecular order ν indicates that the tails are still somewhat flexible and are certainly not completely rigid even at the transition between the S_{A_d} phase and the low-temperature N phase. The small changes in ν (and in η , τ , and ρ) in the N , S_{A_d} , and S_{A_1}

phases in Fig. 5 show that the relative stabilities of these phases are governed by *small* changes in the packing differences of the cores and tails precipitated by small changes in the flexibility of the tails as a function of T .

As seen in Fig. 5, the S_{A_1} - S_{A_d} transition is second order, as evidenced by a continuous change in ρ through the transition and a discontinuity in $\partial\rho/\partial T$ at the transition. In Fig. 5, η and τ also go through a maximum at the S_{A_1} - S_{A_d} transition.

Critical exponents at S_{A_d} - N transitions

In Fig. 6 we look at the power-law dependences of λ and of ρ on the temperature as a second-order S_{A_d} - N transition is approached in different molecular systems. Here, the exponents β and γ^* appear in the following relations:

$$|1-\lambda/\lambda_0| \propto |\Delta T|^\beta, \quad |1-\rho/\rho_0| \propto |\Delta T|^{\gamma^*}, \quad (16)$$

where

$$\Delta T = 1 - T/T_0, \quad (17)$$

and the subscript 0 refers to the transition value.

The values of these exponents are not known *a priori* in the theory of this paper. An inspection of Eqs. (1)–(3) reveals that these exponents cannot be determined analytically in this theory. Therefore, these exponents have been calculated numerically from the values of ρ and λ calculated numerically from the simultaneous solutions (via numerical computer iteration) of Eqs. (1)–(3) at different T .

β is calculated from the S_{A_d} side of the transition, and γ^* is calculated from both sides of the transition. In Fig. 6, $\beta \simeq 0.5$ and $\gamma^* \simeq 1$. Not surprisingly, mean-field exponents are recovered from this mean-field-like model.

The important point, though, from these calculations is the realization that a $\beta \simeq 0.5$ is consistent with the identification of λ (the fraction of positional alignment, or segregated packing) as an "order parameter."¹⁶ This result constitutes a successful test of self-consistency in the original choice of this λ as an order parameter and in the subsequent appearance of λ in the actual molecular packing statistics^{5,6} and resulting equations of this theory.

Concluding remarks

The results in this paper showing that it is not necessary to invoke dipolar forces (or even attractive forces of any kind) to have S_{A_1} , S_{A_d} , and N_R phases should encourage the search for an experimental realization of the results in systems with nonpolar molecules. Experimental progress along this line includes the identification of S_A and N_R phases in binary mixtures of terminal-nonpolar compounds.¹⁷

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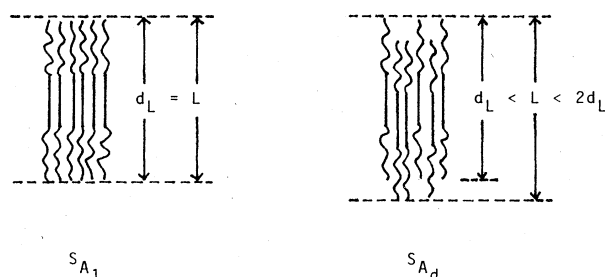


FIG. 7. Schematic diagrams of the relation among the positional alignment of oriented molecules, the layer thickness L , and the molecule length d_L in the S_{A1} and S_{Ad} phases.

APPENDIX A: SCHEMATIC DIAGRAMS OF THE S_{A1} AND S_{Ad} PHASES

Schematic diagrams of the relation among the positional alignment of oriented molecules, the layer thickness L , and the molecule length d_L in the S_{A1} and S_{Ad} phases are shown in Fig. 7 for systems in which each molecule is composed of a rigid rodlike core and two pendent partially flexible tail chains, one at each end of the core.

Several points about the schematic character of these diagrams should be mentioned. (1) The molecules in S_A layers in reality and in the theory of this paper do not all have to be oriented. (See, for example, the values of the core orientational order η in Fig. 5 and the discussion accompanying Fig. 5.) For simplicity, the molecules whose cores are not oriented parallel to the preferred axis of core orientation have not been shown in Fig. 7. (2) The tails are not completely rigid (all-*trans*) in S_A layers in reality or in the theory of this paper (see, for example, the values of the tail intramolecular orientational order ν in Fig. 5 and the surrounding discussion) and are not intended to be interpreted as all-*trans* in Fig. 7. (3) No positional ordering of the centers of mass of the molecules in the directions *perpendicular* to the preferred axis of core orientation exists in S_A layers in reality or in the theory of this paper, and none is intended to exist in Fig. 7. (4) In reality and in the theory of this paper, the molecules have finite breadth (more than the thickness of a line). (5) In reality as well as in the theory of this paper, it is possible for each molecule to have just one tail, or to have two tails (as

shown in Fig. 7). Furthermore, the two tails need not have the same extended length. (6) In the S_{Ad} phase the empty regions in a layer in Fig. 7 caused by the partial, but not total, positional alignment of the molecules in a layer can be filled in reality and in the theory of this paper by empty spaces and/or by parts of molecules from immediately adjacent layers.

APPENDIX B: CALCULATION OF v_0

There are no experimental measurements of v_0 , but it can be estimated from experimental measurements of other quantities in the following manner. The separation distance σ between segment centers at the zero of energy in the Lennard-Jones (12,6) pair potential was taken as 4×10^{-8} cm, an approximate average value for a CH_4 molecule¹⁸ or for a benzene molecule;¹⁸ these chemical species are reasonable approximations for the chemical species in the segments in the tails and cores, respectively, of liquid-crystal molecules. The reduced value ϵ/k of the absolute value of the minimum of energy in a Lennard-Jones (12,6) pair potential is approximately¹⁸ 150 K for CH_4 .

In a simple cubic lattice, $v_\sigma = \sigma^3$, where v_σ is the volume corresponding to the separation distance σ . Using this relation and values of $\sigma = 4 \times 10^{-8}$ cm and $\epsilon/k = 150$ K with an estimate of the reduced hard-repulsive segmental pair-potential energy $U_0 = 1 \times 10^4$ K, a v_0 of 2.98×10^{-23} cm³ was calculated using a Lennard-Jones (12,6) pair potential.

While the hard-repulsive energy U_0 is really infinitely large, a numerical calculation requires a large but *finite* estimate of U_0 . The above estimate of U_0 is reasonable to use here since it gave² good numerical agreement between the experimental values of the temperature^{19,20} and the relative density change¹⁹ at the N - I transition for PAA (*p*-azoxyanisole, or 4,4'-dimethoxyazoxybenzene) and the N - I transition temperature and relative density change calculated for the lattice-theory analog of PAA (i.e., the system in which $r = 4$; $f = 0$; the segmental $\epsilon/k = 300$ K, a value appropriate for a benzene molecule¹⁸ and thus for a core segment; and $\sigma = 4 \times 10^{-8}$ cm) using a lattice theory²¹ with segmental Lennard-Jones (12,6) pair interactions. In the limit that the molecules have only hard repulsions, this lattice theory²¹ is exactly the same for N and I phases as the lattice theory⁶ of this paper here.

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