

Reentrant nematic and multiple smectic-*A* liquid crystals: Intrachain flexibility constraints

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(Received 17 February 1987)

A recent new microscopic, molecular statistical-physics theory for the intrachain constraints on the *n*-alkyl tail-chain flexibility for molecules composed of rigid rodlike cores and *n*-alkyl tail chains in the smectic-*A*₁, smectic-*A*₂, and nematic (including reentrant nematic) liquid-crystal phases and the isotropic liquid phase is used to calculate relative stabilities as well as various thermodynamic and molecular ordering properties (including odd-even effects) for these phases. The molecules can interact via these site-site intermolecular interactions: hard (steric) repulsions, various Lennard-Jones (LJ) potentials for soft repulsions and London dispersion attractions, and/or dipolar forces (dipole-dipole and dipole-induced-dipole). The theoretical results in this paper are in significantly better agreement with experiment than are results in earlier papers using older, more approximate theories. The effects of varying pressure, tail-chain flexibility, and intermolecular interactions on the relative stabilities of the multiple smectic-*A* phases and the reentrant nematic phase are presented. These relative phase stabilities are sensitive to subtle changes in these variables. Predictions and accompanying physical explanations are also made for various systems that have not yet been chemically synthesized and/or studied experimentally.

INTRODUCTION

The partial orientational (and also, in some cases, the partial positional) ordering of molecules that is characteristic of liquid crystals (LC's) occurs frequently in natural and synthetic materials. (See, for example, Ref. 1 for a summary of some of these natural and synthetic systems that have LC ordering, as well as for a discussion of some of the reasons—ranging from very basic physics considerations to very practical applications—for our interest in LC systems.)

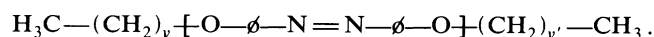
LC's are formed by molecules with highly anisotropic shapes, with these shapes frequently changing as a function of temperature and density. The general purpose of the theory and calculated results in this paper is to identify (predict and explain) the individual components of molecular structure and packing that determine the relative stabilities of the partial orientational and partial positional ordering of the molecules in different LC phases.

New results are reported in this paper for one recent new theory¹ that is a major extension of theories for smectic-*A* (*S*_{*A*}) and reentrant nematic (*N*) phases first reported by this author in 1980 (see Ref. 2). (A reentrant phase occurs when a phase appears in one temperature range, disappears in a lower-temperature range, and then reenters or reappears in an even-lower-temperature range.)

In particular in this paper here, we take a much closer, much more exact look at the effect of the molecule tail-chain flexibility on the stability of multiple *S*_{*A*} and *N* LC phases (including reentrant phases) than in previous papers.³⁻⁶ More specifically, the purpose of this paper is to present results for a recent new theory¹

of describing the *intrachain* constraints on the flexibility of *n*-alkyl (hydrocarbon) tail chains in LC molecules and how these intrachain constraints affect the LC ordering in *N* (including low-temperature *N*—including reentrant *N*) and multiple *S*_{*A*} phases.

An example of a reasonably typical LC molecule structure^{7,8} is



ϕ indicates a *para*-substituted benzene ring; $y, y' \sim 0-20$; y and y' may be equal or unequal. $\text{[-O-}\phi\text{-N=N-}\phi\text{-O-]}$ is the rigid core, and $\text{H}_3\text{C}-(\text{CH}_2)_y-$ and $-(\text{CH}_2)_{y'}-\text{CH}_3$ are the semiflexible tail chains. The overlap of π orbitals in the aromatic, double, and triple bonds in the core section of a LC molecule leads to the rigidity of the core. In the *S*_{*A*} and *N* LC phases and the isotropic liquid (*I*) phase, there is essentially⁹ free rotation of the molecule about the core long axis, thereby giving an effective rodlike, cylindrical shape to the core.^{10,11} The *n*-alkyl tail chains are partially flexible (semiflexible) since it costs a finite, but easily achievable, net energy E_g to make a *trans-gauche* rotation about any carbon-carbon bond between $-\text{CH}_2-$ (methylene) or $-\text{CH}_3$ (methyl) units in a given tail-chain.

It is emphasized that there is an appreciable fraction of *gauche* bonds in *n*-alkyl tail chains in LC and isotropic liquid phases. When each chain is in an all-*trans* state (which in a plane is represented by a zigzag line for each chain), the chains have frozen into the crystalline solid state. Thus, the explicit treatment of the tail-chain flexibility in molecules with *n*-alkyl tails is essential to

differentiate real LC (especially real smectic) phases from crystalline solid phases.

Our purpose of focusing in this paper on new results for a recent new method¹ of describing these intrachain constraints on the tail-chain flexibility is prompted by the following reasons. References 4 and 5 have shown that differences in the steric (hard-repulsive) packing of rigid cores and semiflexible tails—as a function of tail-chain flexibility as a function of temperature—can stabilize S_A [including⁵ smectic- A_1 (S_{A_1}) and smectic- A_d (S_{A_d})] and low-temperature N (including reentrant N) LC phases. It is not necessary to invoke dipolar forces⁶ (or even attractive forces⁶ of any kind) to have these phases.

The steric system results can be understood as follows. In the S_A phases, the differences in the steric packing of the rigid rodlike cores and the semiflexible tail chains are large enough that the oriented molecules positionally align such that cores tend to pack with cores and tails tend to pack with tails. The semiflexible tails bend and twist well around each other, but do not pack as well with the oriented rigid cores.

As T decreases, the tails stiffen somewhat (become less flexible), thus decreasing the packing differences between cores and tails. The need for segregated packing of cores with cores and tails with tails (as in a S_A phase) decreases and is overcome by the entropy of unsegregated packing, leading to a low- T N phase. [The existence of low- T N (specifically, reentrant N) phases is well established experimentally (see, for example, Refs. 12–18).]

These theoretical results in Refs. 4–6 thus explained, for the first time, the following experimental observations: With two or three exceptions,^{8,19} virtually all molecules that form S_A —in fact, that form any kind of smectic (i.e., layered)—LC phases have one or more pendant semiflexible tail chains.^{7,8,20} Furthermore, as the tail chains are shortened, the smectic phases disappear.^{7,8,20}

In these experimental cases, the cores (and hence, any dipoles in the cores) are not sufficient (without the non-polar tails) to stabilize the smectic phases. The semiflexible tail chains provide enough entropy (disorder) to keep the cores from crystallizing totally, thus allowing the existence of the partial positional order in smectic phases.^{3–6}

In Ref. 1, two new microscopic, molecular statistical-physics theories (an exact theory and a simpler, but accurate approximate theory) for the intrachain constraints on the n -alkyl tail-chain flexibility in the S_{A_1} , S_{A_d} , and N LC phases and in the I liquid phase were derived. The new approximate method for calculating these intrachain constraints on the tail-chain flexibility was shown¹ to be remarkably accurate when compared with the exact method. Also, the new approximate method was shown¹ to be computationally *much* faster than the exact method.

Therefore, the new approximate theory was used in Ref. 1 to calculate thermodynamic and molecular ordering properties (including odd-even effects in these properties) for S_{A_1} , S_{A_d} , N , and I phases for a system of molecules composed of rigid rodlike cores and pendant

semiflexible (n -alkyl) tail chains, with cores and tails interacting via various site-site Lennard-Jones potentials (but with *no* dipolar forces). [Odd-even effects are alternations in the magnitudes of thermodynamic and molecular ordering properties (or in the increments between values of these properties) as the number of $-\text{CH}_2-$ and $-\text{CH}_3$ groups in a given n -alkyl tail chain in a molecule varies from odd to even.]

The N phase was found to be somewhat more stable with respect to the S_A phases (particularly at higher temperatures) when using the new approximate flexibility theory in Ref. 1 than when using the old, more approximate flexibility theory of earlier papers.^{3–6} The improved stability of the N phase with respect to the S_A phases in Ref. 1 was shown to be in better general agreement with experiment than were the results of Ref. 6.

The thermodynamic and molecular ordering properties calculated for these phases for this system in Ref. 1 were shown to be in good agreement with experiment. Reference 1 appears to have given the first theoretical treatment of odd-even effects in multiple S_A phases (S_{A_1} and S_{A_d} phases).

This paper here uses the new approximate theory of Ref. 1 to calculate—for the first time—thermodynamic and molecular ordering properties (including odd-even effects) for S_{A_1} , S_{A_d} , N , and I phases for a system of molecules composed of rigid rodlike cores and pendant semiflexible (n -alkyl) tail chains, with the molecules interacting via site-site (segmental) hard (infinitely large) repulsions only or via segmental intermolecular dipolar forces (dipole-dipole forces and dipole-induced-dipole forces) as well as segmental Lennard-Jones potentials [for soft (finite) repulsions and London dispersion attractions]. This paper here also uses the new approximate theory of Ref. 1 to calculate—for the first time—results for low-temperature N (including reentrant N) phases.

There are *no ad hoc* or arbitrarily adjustable parameters in this theory. All input variables are taken from experimental data for atoms or small chemical groups such as benzene rings and methylene groups; all other variables are calculated by the theoretical equations and are found to be reasonable when compared with experimental data for LC's. We do *not* use parameters to fit our calculated results to experimental LC data, since such fitting would obfuscate the identification of the *individual* components of molecular structure (including details of the intrachain constraints on the tail-chain flexibility) and packing that determine the relative stabilities of the partial orientational and partial positional ordering of the molecules in different LC phases.

THEORY

General partition function

The theory¹ that we use here is a localized^{1,3–6} mean-field (LMF) theory for a system of unbranched multisite molecules, where each molecule is composed of a rigid rodlike core and two pendant semiflexible tail chains, one on each end of the core. By *localized* MF theory in this paper, we mean that we have a specific *average*

neighborhood (of other molecular sites and empty space) in a given direction k around a given molecular site in a given local region in the system.^{1,3,4} These local regions are determined by the actual packing of the molecules in the system.

By *multisite*, we emphasize that each molecule in this theory is divided into a series of connected sites. The various sites correspond to various atoms or small groups of atoms (such as a benzene ring or a $-\text{CH}_2-$ group).

We use here a simple-cubic lattice theory.¹ Each molecule has a total of m connected impenetrable cubic segments (sites), each of unit dimension. The total volume of the system includes these impenetrable molecular segments, as well as unoccupied (empty) space or volume.

We have used¹ combinatorial lattice statistics (after the manner of Ref. 3 and references therein) to describe mathematically how the molecules physically pack together under different conditions of pressure, temperature, orientational and positional orderings of the molecules, and particular chemical structures of the molecules (including various site-site intermolecular interactions). We stress that a unique feature of the theory of this paper and Ref. 1 (and of the theories of Refs. 3–6 and 21) is that there are *no ad hoc* or arbitrarily adjustable parameters in these theories.

In particular, the couplings between the orientational and positional orderings of the molecules, the density and temperature of the system, and the specific chemical structure of the molecules arises naturally from the intermolecular and intramolecular packing of the molecules in these theories. We do *not* have to guess at the forms of these couplings, or guess at *ad hoc* coupling constants, or assume artificially simplified forms for these couplings.

For the following five major reasons, we have particular confidence in the practical application of the lattice theory of this paper to LC molecules.

(1) The orientations of any molecule (in fact, the orientation of any segment or bond between segments in any molecule) can be decomposed into its x , y , and z components and mapped directly onto a simple-cubic lattice. (This decomposition of orientations into their x , y , and z components is analogous to normal coordinate analysis in, for example, molecular spectroscopy.) This decomposition and mapping onto a simple-cubic lattice allows us to treat—in a geometrically transparent and mathematically tractable manner—details of molecule chemical structure, including features that are essential in determining the LC ordering of real molecules. A significant number of these features (such as the flexibility of tail chains attached to rodlike cores in LC phases) have not been amenable to treatment by continuum theories.

(2) In the lattice theory of this paper (see below) and Ref. 1 as well as in the lattice theories of Refs. 3–6 and 21, the Gibbs free energy of the system is minimized with respect to the individual x , y , and z components of the orientations of the long axes of the rigid cores of the molecules.

(3) In the lattice theory of this paper (see below) and Ref. 1 as well as in the lattice theories of Refs. 3–6 and

21, the thermodynamic limit is taken (that is, the number of lattice sites M in the system and the number of molecules N_m in the system each go to infinity), and thus the thermodynamic and molecular ordering variables in the system assume a *continuum* of allowed values.

(4) The generalized combinatorial statistics (see Ref. 3) used to derive¹ the analytic partition function [Eq. (1) below] in this paper have been found to be *quite* accurate when compared with Monte Carlo computer simulations²² in at least one limiting case presently amenable to such simulations. (See discussion in Ref. 3.)

(5) The lattice theories of Refs. 3–6 (and references therein)—which form the starting point for the new theory of this paper and Ref. 1—have a well-documented and extremely successful record in *uniquely predicting* new phenomena and *explaining* both existing phenomena (trends, as well as qualitative and quantitative variables) for multisite molecules in LC phases. These lattice theories have been especially effective in relating these predictions and explanations directly to the chemical structures of real LC molecules. These theoretical results have been found to be in good agreement with existing and later experimental data. (See Refs. 3–6 and 21, as well as the review articles of Refs. 23 and 24 and references therein.)

Therefore in this paper and in Ref. 1, the configurational partition function Q (derived from the combinatorial lattice statistics) is given by

$$Q = \Omega \exp[-E_I / (k_B T)], \quad (1)$$

where $\Omega = \Omega(T, \rho, v_0, r, f, E_g, P_{2r}, \lambda)$ and $E_I = E_I(T, \rho, v_0, r, f, E_g, P_{2r}, \lambda, a_\sigma, \epsilon_{cc}, \epsilon_{tt}, \mu_{D\parallel}, \mu_{D\perp}, \alpha_c, \alpha_t)$, where k_B is the Boltzmann constant, and where the molecular and thermodynamic variables in Eq. (1) are defined as follows.

T is the absolute temperature.

ρ is the average density of the system (average fraction of lattice sites occupied by molecular segments); $0 < \rho \leq 1$.

v_0 is the volume of one lattice site (i.e., hard-repulsive volume of one molecular segment).

r and f are the number of rigid segments and semiflexible segments, respectively, in a molecule.

E_g is the energy of a *gauche* rotational state (relative to the *trans* state) of a carbon-carbon bond between methylene or methyl groups in n -alkyl chains.

P_{2r} is the average orientational order of the molecular cores [given by $P_{2r} = \langle (3\cos^2\theta - 1) \rangle / 2$, where θ is the angle between the core long axis and the preferred axis of orientation for the cores (here, axis z); $0 \leq P_{2r} \leq 1$].

λ is the average fraction^{1,3–6} of one-dimensional (1D) *positional* alignment of the centers of mass of the molecules whose cores are oriented parallel to the preferred axis for core orientation; $0 \leq \lambda \leq 1$. [λ in this theory is a real number defined^{1,3–6} in terms of the literal physical packing of the centers of mass of the oriented molecules and thus, in terms of the physical packing of the core and tail parts of the oriented molecules. More specifically, λ is actually the average fraction of the length of a z -axis-oriented molecule that is in register with (positionally aligns with)—in excess of alignments

from random positional packing—the lengths of *z*-axis-oriented neighboring molecules in the *x* and *y* directions, such that cores tend to pack with cores and tails tend to pack with tails for these oriented molecules. (As will be shown later in this paper, λ is thus a reduced ratio between the average layer thickness and the average effective molecule length at a given *T* in a *S_A* phase.)

a_σ is the average separation distance between segment centers at the zero of energy in the Lennard-Jones (12,6) pair potential for any two segments in different molecules.

ϵ_{cc} and ϵ_{tt} are the absolute values of the minimum of energy between two core segments and between two tail segments, respectively, in the Lennard-Jones potential.

$\mu_{D\parallel}$ and $\mu_{D\perp}$ are the longitudinal and transverse, respectively, dipole moments for the molecule (here, for the core).

α_c and α_t are the average polarizabilities for a core segment and a tail segment, respectively.

Equations (1)–(18), (36)–(38), (41), (43), and (45) in this paper are derived in Refs. 3–6. Equations (19)–(35), (39)–(40), (42), and (44) are derived in Ref. 1.

In Eq. (1) for the partition function,

$$(\ln\Omega)/N_m = \left[\sum_{l=R,F} [(Q_{l1}\ln Q_{l1} + 2Q_{l2}\ln Q_{l2} - C_1\ln C_1)C_{l6}/(2\rho)] \right] - C_2 \quad (2)$$

and

$$E_I/N_m = (\rho/9) \left[\sum_{l=R,F} [(Q_{l3}/Q_{l1}) + (Q_{l4}/Q_{l2})]/C_{l6} \right], \quad (3)$$

where

$$Q_{l1} = 1 - [\rho/(3C_{l6})] \{ (1 + 2P_{2r})[(r-1) + q\lambda C_4] + (1 + 2P_{2r}P_{2i})f \}, \quad (4)$$

$$Q_{l2} = 1 - [\rho/(3C_{l6})] \{ (1 - P_{2r})(r-1) + (1 - P_{2r}P_{2i})f - q(1 + 2P_{2r})\lambda C_5 \}, \quad (5)$$

$$Q_{l3} = (1 - P_{2r})^2 [W_3 + (r-2)^2\omega_{cc\parallel} + 2(r-2)A_1\omega_{ct} + A_1^2\omega_{tt}] + (1 - P_{2r})(1 + 2P_{2r}) \{ (B_1 + q\lambda B_2)[2(r-2)\omega_{ct} + A_1\omega_{tt}] + [(1 + 2P_{2r})(B_1 + q\lambda B_2)]^2\omega_{tt}/2 \}, \quad (6)$$

$$Q_{l4} = (1 - P_{2r})^2 \{ W_3 + B_1[2(r-2)\omega_{ct} + A_1\omega_{tt}] + B_1^2\omega_{tt} \} + (1 - P_{2r})(1 + 2P_{2r}) \{ 2[(r-2)^2(1 + q\lambda)\omega_{cc\parallel} + (r-2)[(1 + q\lambda)A_1 + (A_1 + q\lambda A_2)]\omega_{ct} + A_1(A_1 + q\lambda A_2)\omega_{tt} \} + B_1[2(r-2)(1 + q\lambda)\omega_{ct} + (A_1 + q\lambda A_2)\omega_{tt}] + (1 + 2P_{2r})^2 \{ [(r-2)(1 + q\lambda)]^2\omega_{cc\parallel} + 2(r-2)(1 + q\lambda)(A_1 + q\lambda A_2)\omega_{ct} + (A_1 + q\lambda A_2)^2\omega_{tt} \}, \quad (7)$$

$$C_1 = 1 - \rho, \quad (8)$$

$$C_2 = \{ [(1 + 2P_{2r})\ln(1 + 2P_{2r}) + 2(1 - P_{2r})\ln(1 - P_{2r})]/3 \} + \left[\sum_{l=R,F} \{ \ln[\rho/(3C_{l6})] \} / 2 \right], \quad (9)$$

$$C_3 = r - 1 + P_{2i}f, \quad (10)$$

$$C_4 = r - [(1 + 2P_{2i})f/3], \quad (11)$$

$$C_5 = (1 - P_{2i})f/3, \quad (12)$$

$$C_{l6} = m + q[(1 + 2P_{2r})\lambda(r-f)/3], \quad (13)$$

$$W_3 = (r-2)^2\omega_{cc\parallel} + 2(r-2)A_1\omega_{ct} + A_1^2\omega_{tt}, \quad (14)$$

$$A_\xi = 2 + x[f(2 + P_{2i})/3], \quad (15)$$

$$B_\xi = 1 + x[2f(1 - P_{2i})/3]. \quad (16)$$

In Eqs. (15) and (16) $x = +1$ if $\xi = 1$; $x = -1$ if $\xi = 2$. If $l = R$ in Eqs. (2)–(16) above, then $q = +1$; if $l = F$, then $q = -1$.

In the above equations,

$$m = (r + f); \quad (17)$$

N_m is the number of molecules in the system; *R* and *F* refer to potentially core-rich local regions and potentially tail-rich local regions, respectively, in the system; and P_{2i} is the average tail *intramolecular* orientational order (i.e., a measure of the average stiffness of the tails) where by analogy to P_{2r} ,

$$P_{2i} = \langle (3 \cos^2\psi - 1) \rangle / 2 = 1 - 3u, \quad (18)$$

and ψ is the angle between a given tail bond and the long axis of the core of the molecule to which the tail bond is attached. $0 \leq P_{2i} \leq 1$.

The total fraction $2u$ of tail bonds bent out of the direction of the core long axis of a molecule is given by

$$2u = \left[\sum_\gamma 2u_\gamma f_\gamma \right] / \left[\sum_\gamma f_\gamma \right], \quad (19)$$

where f_γ is the number of semiflexible segments ($-\text{CH}_2-$ or $-\text{CH}_3$ groups) in tail chain γ of the mol-

ecule, and $2u_\gamma$ is the total fraction (with u_γ parallel to each of the two simple-cubic axes) of semiflexible segment bonds (C—C bonds) bent out of the direction of the core long axis in tail chain γ . Here $\gamma=1$ or 2. Also,

$$f = \sum_{\gamma} f_{\gamma} . \quad (20)$$

Each semiflexible tail bond has three choices of direction, which mimic the three choices [*trans*, *gauche* (+), *gauche* (−)] of rotation (specifically, rotational energy minima) about carbon-carbon bonds between methylene (or methyl) groups in the tetrahedral coordination in a *n*-alkyl tail chain. A *trans* tail choice has a Boltzmann statistical weight of

$$\zeta_1 = 1/(1+2\Lambda) , \quad (21)$$

and each *gauche* choice has a Boltzmann statistical weight of

$$\zeta_2 = \Lambda/(1+2\Lambda) , \quad (22)$$

where

$$\Lambda = \exp[-E_g/(k_B T)] . \quad (23)$$

For an all-*trans* sequence on a simple-cubic lattice, the long axis of the tail chain is parallel to (literally, an extension of) the long axis of the core of the molecule. Sequences of *gauche* (\pm) *gauche* (\mp) are energetically very unfavorable^{25,26} and therefore are not allowed^{1,26} in this paper.

For $f_\gamma=1$ in this paper as in Ref. 1, $2u_\gamma$ in Eq. (19) is given by

$$2u_\gamma = 2u_1 = 2\zeta_2 . \quad (24)$$

For $f_\gamma \geq 2$ in this paper using the new approximate method of Ref. 1, $2u_\gamma$ in Eq. (19) is given by

$$2u_\gamma = \left[\left[\sum_{j=1}^2 Y_{1j} \right] + [(f_\gamma - 2)/2] \left[\sum_{j=1}^2 Y_{2j} \right] \right] / f_\gamma , \quad \text{even } f_\gamma \geq 2 \quad (25)$$

and

$$2u_\gamma = \left[\left[\sum_{j=1}^3 Y_{3j} \right] + [(f_\gamma - 3)/2] \left[\sum_{j=1}^2 Y_{2j} \right] \right] / f_\gamma , \quad \text{odd } f_\gamma \geq 2 . \quad (26)$$

In Eqs. (25) and (26),

$$Y_{11} = 2(\zeta_1 \zeta_2 + \zeta_2^2)/D_1 , \quad (27)$$

$$D_1 = \zeta_1^2 + 4\zeta_1 \zeta_2 + 2\zeta_2^2 , \quad (28)$$

$$Y_{12} = 2(2\zeta_1 \zeta_2 + \zeta_2^2)/D_1 , \quad (29)$$

$$Y_{21} = Y_{22} = 2(\zeta_1^2 + 3\zeta_1 \zeta_2 + 2\zeta_2^2)/D_2 , \quad (30)$$

$$D_2 = 3\zeta_1^2 + 2(5\zeta_1 \zeta_2 + 3\zeta_2^2) , \quad (31)$$

$$Y_{31} = 2(\zeta_1^2 \zeta_2 + 3\zeta_1 \zeta_2^2 + \zeta_2^3)/D_3 , \quad (32)$$

$$D_3 = \zeta_1^3 + 2(3\zeta_1^2 \zeta_2 + 4\zeta_1 \zeta_2^2 + \zeta_2^3) , \quad (33)$$

$$Y_{32} = 2(2\zeta_1^2 \zeta_2 + 4\zeta_1 \zeta_2^2 + \zeta_2^3)/D_3 , \quad (34)$$

$$Y_{33} = 6(\zeta_1^2 \zeta_2 + \zeta_1 \zeta_2^2)/D_3 , \quad (35)$$

The one-dimensional (1D) positional alignment of the centers of mass (and thus, of the rigid cores) of the 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 tail-rich regions (labeled *F*) in each layer. When $\lambda=0$, these regions have the same segmental composition (i.e., composition of cores and tails) and there is no layering. A S_A phase of some kind exists for any value of λ for which $0 < \lambda \leq 1$.

Each ω_{yz} is an average intermolecular pair interaction energy between a *y*-type segment and a *z*-type segment, where $y=c$ or *t* and $z=c$ or *t*; *c* and *t* indicate *core* and *tail*, respectively. \parallel and \perp indicate segments that are attached to cores that are parallel and perpendicular, respectively, to each other. $\omega_{ct\parallel} = \omega_{ct\perp} = \omega_{ct}$; $\omega_{tt\parallel} = \omega_{tt\perp} = \omega_{tt}$; and

$$\omega_{yz} = \sum_{j=1}^3 \omega_{yzj} , \quad (36)$$

where $j=1$ refers to Lennard-Jones (12,6) interactions, $j=2$ refers to dipole-induced-dipole interactions, and $j=3$ refers to dipole-dipole interactions;

$$\omega_{yz1} = 4\epsilon_{yz} [(a_\sigma/a)^{12} - (a_\sigma/a)^6] ; \quad (37)$$

$\omega_{cc\parallel} = \omega_{cc\perp}$. Here, $\epsilon_{cc}/k=300$ K and $\epsilon_{tt}/k=150$ K. These values are appropriate for benzene and methane molecules,^{27(a)} respectively, which are reasonable approximations for the chemical species in the core and tail segments, respectively, of typical LC nondipolar molecules; $\epsilon_{ct} = (\epsilon_{cc} \epsilon_{tt})^{1/2}$.

Here, $a_\sigma = 4 \times 10^{-8}$ cm, an approximate average value appropriate for a methane or benzene molecule.^{27(a)} a is the average separation distance between the centers of two first-neighbor intermolecular segments and is calculated here (as in Refs. 1 and 6) from ρ using

$$\rho = mv_0/v , \quad v = a^2[2a + v_0^{1/3}(m-2)] , \quad (38)$$

where v is the average volume associated with one molecule, and $v_0 = 2.98 \times 10^{-23}$ cm³, as estimated⁵ from experimental measurements of various quantities.

ω_{yz2} and ω_{yz3} are calculated (after the manner of Refs. 1 and 6) using Eqs. (13.5-3) and (1.3-8), respectively, of Ref. 27(b) using values of $\mu_{D\parallel}$, $\mu_{D\perp}$, α_c , and α_t estimated from experimental bond and group dipole moments^{28(a),29} and polarizabilities.^{28(b)} Here, $\mu_{D\parallel} = 5.2D$, $\alpha'_c = \alpha_c(r-2) = 24 \times 10^{-24}$ cm³, and $\alpha_t = 2 \times 10^{-24}$ cm³; ($r-2$) is the number of rigid segments having core-type interactions.^{1,6,21} Here, $\mu_{D\parallel}$ and α_c are values appropriate^{1,6} for a core with relatively large dipolar forces, of the order of those in a cyanobiphenyl-oxy-type core, and α_t is a value appropriate^{1,6} for a methylene group.

As in Ref. 1 (after the manner of Ref. 6),

$$\omega_{cc2\parallel} = \omega_{cc2\perp} = -(\mu_{D\parallel}^2 + \mu_{D\perp}^2)\alpha_c / [a^6(r-2)^2] \quad (39)$$

and

$$\omega_{ct2} = -(\mu_{D\parallel}^2 + \mu_{D\perp}^2)\alpha_t / [2a^6(r-2)^2]. \quad (40)$$

Also,

$$\omega_{cc3\parallel} = -\mu_{D\parallel}^2 / \{2[a(r-2)]^3(1 + \chi q \lambda)\}, \quad (41)$$

where $\chi = 1$ for $\omega_{cc3\parallel}$ in Eq. (7) and $\chi = 0$ for $\omega_{cc3\parallel}$ in Eq. (14);

$$\omega_{cc3\perp} = -\mu_{D\perp}^2 / \{2[a(r-2)]^3\}. \quad (42)$$

Also, $\omega_{tt2} = \omega_{ct3} = \omega_{tt3} = 0$.

If $\mu_{D\perp} = 0$ (as in Ref. 6 and in this paper here), we are dealing only with the effect of longitudinal dipoles. The above equations used for the dipole-dipole interactions explicitly take into account (1) whether the longitudinal dipoles (in the cores) are perpendicular (which occurs when the cores are perpendicular) or (2) whether the longitudinal dipoles are parallel or antiparallel (opposed) when the cores are aligned (parallel), as well as the degree of positional alignment of the cores (and thus of the dipoles).

In this paper, $r = 4$, as estimated^{10(a),30} from experimental data for typical length-to-breadth ratios of the rigid cores of real LC molecules. Also in this paper, $E_g/k = 250$ K or 400 K, the approximate lower and upper limits (as estimated²⁵ from experimental data) for the *trans-gauche* energy difference in typical *n*-alkyl chains.

Using the partition function

Various thermodynamic equations are obtained (after the manner of Refs. 4 and 21) from the partition function Q , including (1) a pressure-volume-temperature (PVT) equation of state, and (2) and (3) equations that minimize the Gibbs free energy G of the system with respect to P_{2r} and λ , respectively, at constant P and T . Within the physical constraints $0 < \rho \leq 1$, $0 \leq P_{2r} \leq 1$, and $0 \leq \lambda \leq 1$, these three specific equations are (in general) solved simultaneously (via numerical computer iteration) to obtain the numerical values of ρ , P_{2r} , and λ in the various phases of the system at given P and T .

In practice¹ in the following two cases, the calculations with this theory are *much* easier and faster if we choose T instead of another variable as one of the unknowns in these calculations. (1) For the S_{A_d} phases (where $0 < \lambda < 1$), the calculations are much faster if T is an unknown for a given P and λ . (2) In locating a transition between two phases 1 and 2 at given P , the calculations are considerably faster if T is an unknown with the condition $\mu_1 = \mu_2$ (where μ_i is the chemical potential of phase i at the transition).

There are *no ad hoc* or arbitrarily adjustable parameters in this theory. All input variables are taken from experimental data for atoms or small chemical groups such as benzene rings and methylene groups (see earlier); all other variables are calculated by the theoretical equations and are found to be reasonable when compared with experimental data.

By the physical definitions of the various phases, $P_{2r} = 0$ in the I phase, and $0 < P_{2r} \leq 1$ in the N and S_A phases. $\lambda = 0$ in the I and N phases.

The S_{A_1} and S_{A_d} phases are physically defined¹⁸ by the following relations between the layer thickness L and the molecule length d_L . $L = d_L$ in the S_{A_1} phase and $d_L < L < 2d_L$ in the S_{A_d} phase.

Physically,⁵ the only way to have a S_{A_1} phase (i.e., to have $L = d_L$) 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.

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 paper is given¹ by

$$L = d_L + (1 - \lambda)d_L = (2 - \lambda)d_L, \quad (43)$$

$$d_L = v_0^{1/3} \{r + f[(1 + 2P_{2r})/3]\} + (a - v_0^{1/3}). \quad (44)$$

In contrast to Refs. 4–6, d_L and thus L in Ref. 1 and this paper are given in the units of $v_0^{1/3}$ and also include the empty space $(a - v_0^{1/3})$ between the hard-repulsive ends of two molecules along the z axis. In the S_{A_1} phase, this empty space is simply the space between the hard-repulsive ends of two molecules in adjacent layers. (The phase diagrams, etc., in Refs. 3–6 are unchanged, since they were all actually calculated using the basic variable λ , rather than the derivative variables L and d_L .)

RESULTS AND DISCUSSION

Some early results using the theory of this paper were presented by this author in 1985. (See Ref. 31).

Results calculated using the theory of the preceding "Theory" section are presented in this paper here for the relative stabilities of S_{A_1} , S_{A_d} , and N (including low-temperature N , including reentrant N) LC phases and I liquid phases for three representative classes of systems: (1) steric systems: all $\omega_{yz} = 0$ (thus, $E_I = 0$), and the molecules interact via only hard repulsions; (2) Lennard-Jones (LJ) systems with no dipolar forces: all $\omega_{yz2} = \omega_{yz3} = 0$; and (3) LJ systems with dipolar forces, including dipole-dipole forces and dipole-induced-dipole forces. While these three systems differ in intermolecular interaction energies (i.e., in ω_{yz} 's and thus E_I), all three systems have a finite nonzero *intra*chain *trans-gauche* energy difference E_g/k (with $E_g/k = 250$ K or 400 K, as discussed in the preceding section).

In the systems studied in this paper, $f_1 = 4$ [where f_1 is the number of segments (or $-\text{CH}_2-$ or $-\text{CH}_3$ groups) in tail chain 1 in each molecule in the system].

Also in this paper, the pressure $P=1$ atm, except for the steric systems (in which $P>1$ atm). As is well known,^{4-6,21} condensed phases can only exist at higher pressures and/or lower temperatures in theories or systems in which the molecules interact only through hard-repulsive forces than in theories or systems in which the molecules also interact through attractive forces.

In the particular calculations whose results are shown in the figures of this paper, these phase transitions were found to be second order: S_{A_d} - N (except as noted), and S_{A_1} - S_{A_d} . In these calculations, these phase transitions were found to be weakly first order: N - I , S_{A_d} - I , and S_{A_1} - I .

Improved phase diagrams for all systems with new approximate flexibility theory

In Figs. 1-3, the relative stabilities of S_{A_1} , S_{A_d} , N , and I phases are presented as a function of the temperature T and the number f_2 of segments (or $-\text{CH}_2-$ or $-\text{CH}_3$ groups) in tail chain 2 for $E_g/k=250$ K. $P=198$ atm for the steric system in Fig. 1. Figures 2 and 3 show results (at $P=1$ atm) for the LJ nondipolar system and the LJ dipolar system, respectively.

The results in Figs. 1-3 in this paper calculated using the new approximate theory for the intrachain constraints on the n -alkyl tail-chain flexibility can be compared with the results in Figs. 1-3 of Ref. 6 using the old, more approximate theory for tail-chain flexibility. [In making these comparisons, recall from Eq. (20) that $f=f_1+f_2=4+f_2$ in Figs. 1-3 in this paper.]

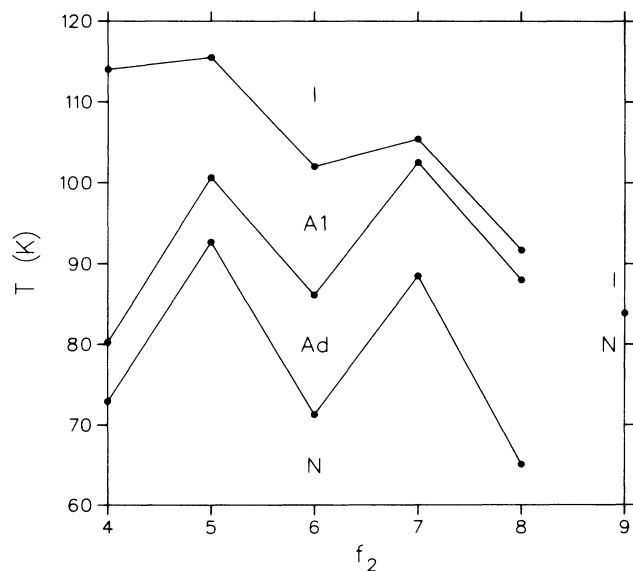


FIG. 1. Phase transition temperatures T (indicated by solid circles) vs the number f_2 of segments in tail chain 2 for the steric system with $E_g/k=250$ K and $P=198$ atm. The phase names are abbreviated as isotropic (I), nematic (N), smectic- A_1 (A_1), and smectic- A_d (A_d). The solid lines connecting the circles have been drawn to aid the eye in observing odd-even effects.

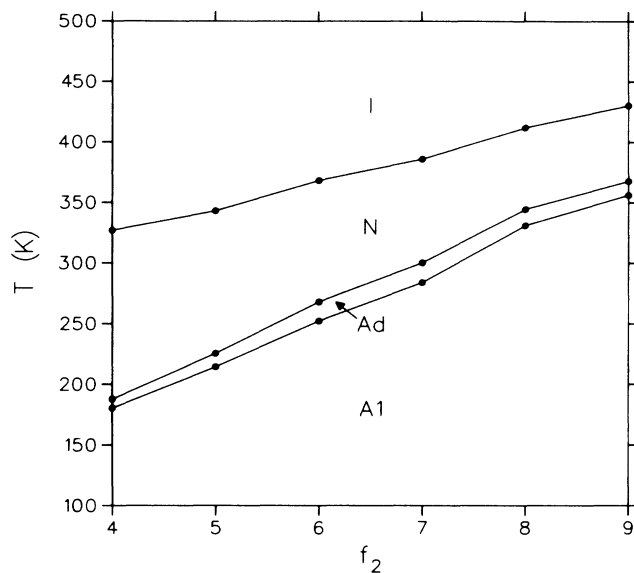


FIG. 2. Phase transition temperatures vs the number of segments in tail chain 2 for the Lennard-Jones nondipolar system for $E_g/k=250$ K. The symbols and the solid lines are as defined in Fig. 1.

The *first major result* is (as expected) that the LC phases are stable at higher temperatures in Figs. 1-3 of Ref. 6 than in the corresponding systems in Figs. 1-3 of this paper. This result is due to that fact that the tail chains are stiffer—i.e., have fewer segments $2u$ [see Eq. (19)] bent out of the core long axis of the molecule [see also Figs. 1(a)-1(c) and accompanying discussion in Ref.

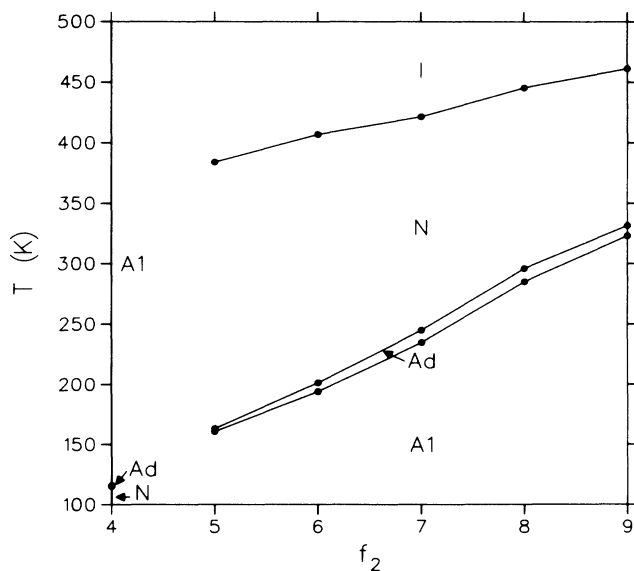


FIG. 3. Phase transition temperatures vs the number of segments in tail chain 2 for the Lennard-Jones dipolar system for $E_g/k=250$ K. The symbols and the solid lines are as defined in Fig. 1.

1]—and thus help stabilize orientational LC ordering of the cores (i.e., P_{2r} is larger) at higher temperatures with the old (less accurate) approximate flexibility theory used in Ref. 6 than with the new (more accurate) approximate flexibility theory of Ref. 1 used in this paper.

A comparison of Figs. 4 and 5 for the LJ nondipolar system with $f_2=5$ further illustrates the result that the tail chains are stiffer [P_{2i} in Eq. (18) is larger] and that the LC phases are stable at higher temperatures in the systems calculated (as in Fig. 4) using the old approximate flexibility theory of Ref. 6 than in the corresponding systems calculated (as in Fig. 5) using the new approximate theory in this paper here. Note that P_{2i} increases with decreasing T [see Eqs. (18)–(35)] and that P_{2i} for lower T in Fig. 5 is smaller than P_{2i} for higher T in Fig. 4.

Figures 4 and 5 also show the average values of the density ρ , the 1D positional order λ of the molecules, the intermolecular orientational order P_{2r} of the cores of the molecules, and the *intermolecular* orientational order P_{2f} of the tails of the molecules as a function of T . The tail intermolecular orientational order P_{2f} is the tail analog of P_{2r} and is given^{1,4–6,21} by

$$P_{2f} = P_{2r} P_{2i} . \quad (45)$$

The *second major result* seen when comparing the systems in Figs. 1–3 in this paper with the corresponding systems in Figs. 1–3 in Ref. 6 is that there are odd-even effects seen in the transition T calculated using the new approximate flexibility theory of this paper here, while

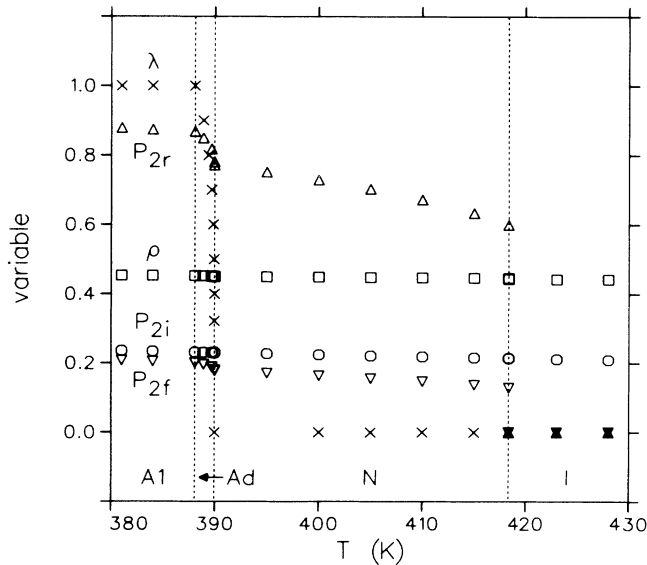


FIG. 4. Molecular ordering and thermodynamic variables λ , P_{2r} , P_{2f} , P_{2i} , and ρ as a function of temperature in different phases for $f_2=5$ for the LJ nondipolar system calculated using the old approximate flexibility theory of Ref. 6 with $E_g/k=250$ K. The dotted lines denote phase boundaries at constant T . The phase name abbreviations are as defined in Fig. 1.

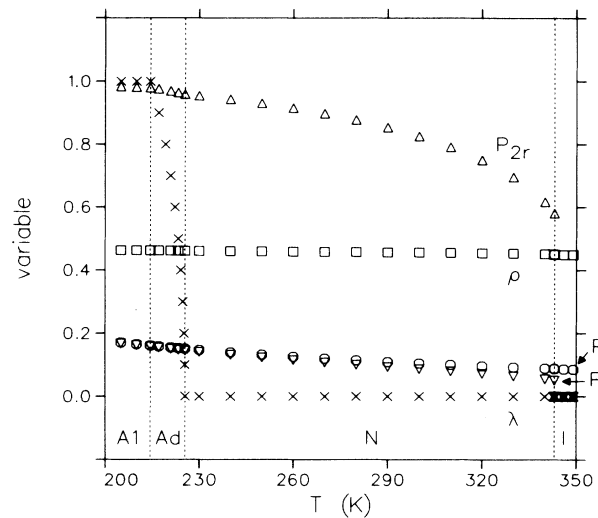


FIG. 5. Molecular ordering and thermodynamic variables λ , P_{2r} , P_{2f} , P_{2i} , and ρ as a function of temperature in different phases for $f_2=5$ for the LJ nondipolar system calculated using the new approximate flexibility theory of this paper (and Ref. 1) with $E_g/k=250$ K. The dotted lines are defined as in Fig. 4, and the phase name abbreviations are as defined in Fig. 1.

there are no odd-even effects generated using the old approximate flexibility theory of Ref. 6. Although not shown here in this paper, odd-even effects are seen in the other thermodynamic and molecular ordering properties in the three systems in Figs. 1–3 and 6 in this paper here. (Some of these odd-even effects in other properties

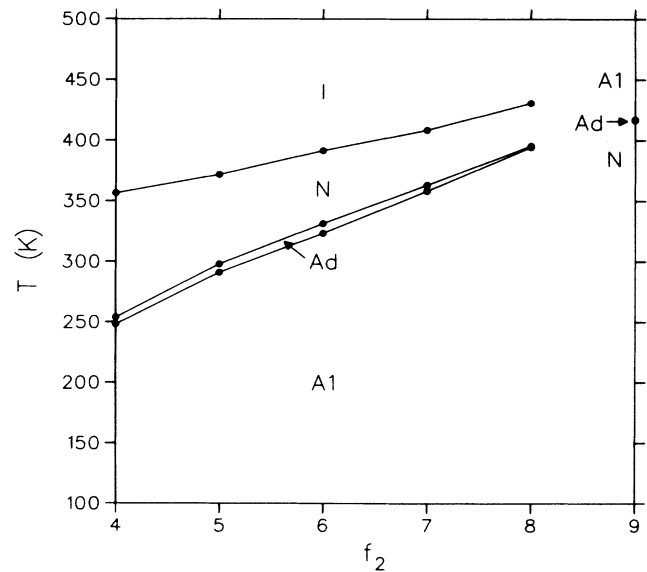


FIG. 6. Phase transition temperatures vs the number of segments in tail chain 2 for the Lennard-Jones nondipolar system for $E_g/k=400$ K. (The S_{Ad} -N transition for $f_2=8$ here is weakly first order.) The symbols and the solid lines are as defined in Fig. 1.

for the LJ nondipolar system in Fig. 2 in this paper here have been plotted in Figs. 4–9 of Ref. 1.)

For some transitions in Figs. 1–3 and 6 in this paper here, curves drawn through the values for the various transition temperatures for even f_2 (i.e., for tail chain 2 with even numbers of carbon atoms) are higher (at larger magnitudes) than the curves for odd f_2 . The reverse trend is seen for other transitions in these figures in this paper. Both cases (“evens high” and “odds high”) for transition T are seen experimentally (see, for example, Refs. 7, 8, 20, and 32), in the same system and in different systems. There is some tendency in these experimental systems (as in the results calculated in this paper here) to see “evens high” for systems with higher transition T and to see “odds high” for systems with lower transition T .

In general, the magnitudes of the odd-even effects due to the *intrachain* constraints on the tail-chain flexibility in this paper appear to be a little smaller than the magnitudes of the odd-even effects in experimental measurements in LC systems (see, for example, Refs. 7, 8, 20, and 32). While this result indicates that *intermolecular* constraints on the tail-chain flexibility also make some contribution to the odd-even effects seen experimentally, the purpose of this paper here is to isolate and focus on contributions from *intrachain* constraints.

[In another paper³³ to be published, the more difficult problem of treating contributions from *intermolecular* constraints on the tail-chain flexibility is addressed in an explicit manner using (as in this paper here) *no ad hoc* or arbitrarily adjustable parameters. Some early results from this new theory for *intermolecular* constraints were presented by this author in 1986 (see Ref. 34).]

The *third major result* seen when comparing Figs. 2 and 3 in this paper with the corresponding systems in Figs. 2 and 3 in Ref. 6 is that the N phase is somewhat more stable with respect to the S_A phases (particularly at higher temperatures) in the LJ systems (both nondipolar and dipolar systems) when the new approximate flexibility theory is used in this paper here than when the old approximate flexibility theory is used in Ref. 6. This improved stability of the N phase with respect to the S_A phases in this paper here is in better general agreement with experiment (see, for example, Refs. 7, 8, and 20) than are the results of Ref. 6.

The *fourth major result* seen when comparing the LJ systems in Figs. 2 and 3 in this paper with the corresponding systems in Figs. 2 and 3 in Ref. 6 is that the conditions for low- T N (including reentrant N) phases occur less frequently with the new approximate flexibility theory of this paper here than with the old approximate flexibility theory of Ref. 6. This decrease in the frequency of conditions for low- T N (including reentrant N) phases in this paper here is in better general agreement with experiment (see, for example, Refs. 7, 8, 12–18, and 20).

In the LJ nondipolar system shown in Fig. 2 of this paper here, there are no low- T N phases. In the LJ dipolar system shown in Fig. 3 of this paper here, conditions for a reentrant N phase exist in the phase space between $f_2=4$ and $f_2=5$, since there is an N phase stable

at lower T than the S_A phases for $f_2=4$ and an N phase stable at higher T than the S_A phases for $f_2=5$. [While noninteger values of f_2 are not available experimentally in pure (single-component) LC systems, effective noninteger f_2 values are easily achieved experimentally in a mixture of LC components with different integer values of f_2 . In fact, reentrant N phases were first seen experimentally (see Ref. 12) in mixtures of LC components before these phases were seen in pure LC systems.]

N reentrance: Varying the pressure, flexibility, or intermolecular interactions

As seen in Table I, a reentrant N phase can be generated in the steric system of Fig. 1 by decreasing the pressure to $P=149$ atm and increasing the *trans-gauche* energy difference to $E_g/k=400$ K. These trends with decreasing P and increasing E_g/k in the steric system here can be understood as follows.

In some T ranges, the flexibility of the tail chains is large enough and the density ρ of the system is large enough that the phases of lowest Gibbs free energy are the S_A phases in which the molecules positionally align such that rigid rodlike cores of oriented molecules tend to pack with other rigid cores while the semiflexible tail chains tend to pack with other semiflexible tail-chains. (The semiflexible tail chains bend and twist well around each other, but do not pack as well with the oriented rigid cores.)

As T decreases, the tails stiffen somewhat [become less flexible—see Eqs. (18)–(35)], thus decreasing the pack-

TABLE I. Stable phases, transition temperatures, and transition densities for the steric system for $f_2=8$ with varying values of pressure P and *trans-gauche* energy difference E_g/k . The phase names are abbreviated as isotropic (I), nematic (N), smectic- A_1 (S_{A_1}), and smectic- A_d (S_{A_d}). [The S_{A_d} - N transition (transition to higher-temperature N phase) for $P=149$ atm and $E_g/k=400$ K is weakly first order.]

$P=198$ atm, $E_g/k=250$ K							
	N	65.1 K	S_{A_d}	88.0 K	S_{A_1}	91.7K	I
$\rho=$		0.789		0.739		0.704(I)	0.727(S_{A_1})
$P=149$ atm, $E_g/k=250$ K							
	N	57.3 K	S_{A_d}	63.6 K			I
$\rho=$		0.756		0.721(I)			0.737(S_{A_d})
$P=198$ atm, $E_g/k=400$ K							
	N	82.6 K	S_{A_d}	88.9 K			I
$\rho=$		0.739		0.711(I)			0.725(S_{A_d})
$P=149$ atm, $E_g/k=400$ K							
	N	67.5 K	S_{A_d}	70.1 K	N	71.5 K	I
$\rho=$		0.721		0.711(N)		0.696(I)	
				0.713(S_{A_d})		0.706(N)	

ing differences between cores and tails. The need for segregated packing of cores with cores and tails with tails (as in a S_A phase) decreases and is overcome by the entropy of unsegregated packing, leading to a low- T N phase.

Decreasing P decreases ρ (see Table I) and decreases the size of the T range of the S_A phases more than the size of the T range of the N phase. At smaller ρ , there is more volume in the system to accommodate positional disorder as in the N phase and to accommodate positional and orientational disorder as in the I phase. The phases with increased molecular disorder are stabilized by the increased entropy associated with this disorder.

As E_g/k increases in the steric system here, the tail chains become stiffer and thus help stabilize orientational LC ordering of the cores at higher T . The density of the system is smaller (see Table I) at these higher T , thus making the size of the T range of the S_A phases decrease more than the size of the T range of the N phase (see the density arguments in the preceding paragraph).

In summary, there are S_A phases and a low- T N phase in the steric system in Fig. 1. As seen in Table I, decreasing P and increasing E_g/k in the steric system of Fig. 1 decreases the size of the T range of the S_A phases, especially at the higher- T end. This result sets up conditions for the existence of a stable high- T N phase (see Table I), thus making the low- T N phase a reentrant N phase. [The existence of low- T N (specifically, reentrant N) phases is well established experimentally (see, for example, Refs. 12–18).]

As seen in Fig. 6, conditions favoring reentrant N behavior can be generated in the LJ nondipolar system of Fig. 2 by increasing E_g/k to 400 K. There are S_A phases and a high- T N phase in the LJ nondipolar system in Fig. 2. As seen in Fig. 6, conditions for a reentrant N phase exist in the phase space between $f_2=8$ and $f_2=9$, since there is an N phase stable at higher T than the S_A phases for $f_2=8$ and an N phase stable at lower T than the S_A phases for $f_2=9$.

As E_g/k increases in the LJ nondipolar system, the tail chains become stiffer [see Eqs. (18)–(35)] and thus help stabilize orientational LC ordering of the cores at higher T . Increasing E_g/k in the LJ nondipolar system increases ρ of the system slightly at the same T (compare Figs. 5 and 7), thus making the size of the T range of the S_A phases increase more than the size of the T range of the N phase for $f_2 \leq 8$ in Fig. 6. (Recall the discussion earlier regarding the relationship between ρ and the relative size changes of the T range of the S_A phases and the T range of the N phase.) The greater relative increase in the size of the T range of the S_A phases in Fig. 6 is seen at the higher- T end of the T range of the S_A phases.

At the lower- T end of the T range in the S_A phases in Fig. 2, the following phenomena occurs as E_g/k increases (see Fig. 6) for $f_2=9$. Since the tail chains are stiffer at larger E_g/k , there is thus less difference between the packing of the rigid cores and the packing of the tail chains at lower T . Thus, the need for segregated packing of cores with cores and tails with tails (as in a S_A phase) decreases and is overcome by the entropy of

unsegregated packing, leading to a low- T N phase. Between $f_2=8$ and $f_2=9$ in Fig. 6, the conditions exist for this low- T N phase to be a reentrant N phase.

A comparison of Figs. 5 and 7 for the LJ nondipolar system with $f_2=5$ further illustrates the result that the tail chains are stiffer [P_{2i} in Eq. (18) is larger] and thus that the LC phases are stable at higher temperatures for $E_g/k=400$ K (Fig. 7) than for $E_g/k=250$ K (Fig. 5). (Figures 5 and 7 also show the average values of ρ , λ , P_{2r} , and P_{2f} as a function of T .)

Due primarily to the soft (finite) repulsions (actually to the net effect of the soft repulsions and the London dispersion attractions) in the LJ forces, the molecules interact (“feel”) each other at larger separation distances in the LJ system than in the steric system. This situation allows a subtle competition (see Figs. 2 and 6) between energy and entropy in determining the relative stabilities of the S_A phases and the N phases at different T and f_2). The differences in the LJ energies between cores and tails (cf. ϵ_{cc} to ϵ_{tt}) favor the segregated packing (cores with cores, and tails with tails) of the S_A phases. The entropy of unsegregated packing (positional disorder) favors the N phase.

As seen in Figs. 5 and 7 and Table I, the densities in the S_A and N phases are smaller in the LJ system than in the steric system due to the fact that the molecules interact (“feel”) each other at larger separation distances in the LJ system than in the steric system. This difference in the magnitude of ρ between the LJ system and the steric system leads to the slightly different response (seen above) in ρ of the two systems when E_g/k is increased.

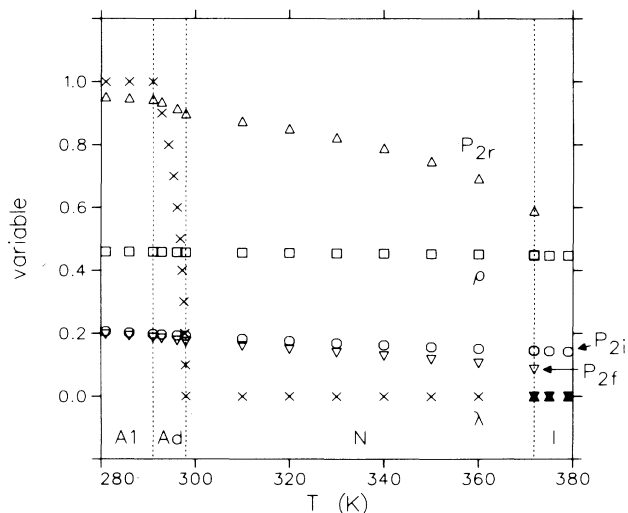


FIG. 7. Molecular ordering and thermodynamic variables λ , P_{2r} , P_{2f} , P_{2i} , and ρ as a function of temperature in different phases for $f_2=5$ for the LJ nondipolar system calculated using the new approximate flexibility theory of this paper (and Ref. 1) with $E_g/k=400$ K. The dotted lines are defined as in Fig. 4, and the phase name abbreviations are as defined in Fig. 1.

In the steric system of Fig. 1, increasing E_g/k decreases ρ . In contrast, in the LJ nondipolar system of Fig. 2, increasing E_g/k increases ρ slightly. As E_g/k increases, the tail chains get stiffer and thus help stabilize orientational LC ordering of the cores at higher T .

At the relatively larger ρ 's of the steric system, the molecules with stiffer tail chains do not pack as well (as efficiently) as the molecules did with more flexible tail chains, and thus ρ of the system decreases as E_g/k increases. At the relatively smaller ρ 's of the LJ system, the increase in the orientational alignment of the cores with the stiffer tail chains leads to slightly more efficient packing of the molecules and thus to a slight increase in ρ as E_g/k increases.

As seen earlier in Fig. 3 (see the fourth major result in the preceding section "Improved phase diagrams. . ." of the discussion), conditions favoring reentrant N behavior can also be generated in the LJ nondipolar system of Fig. 2 by adding dipolar forces. This behavior can be understood as follows.

A comparison of Figs. 5 and 8 for $f_2=5$ show that the addition of dipolar forces in Fig. 8 to the LJ nondipolar system of Fig. 5 orients the cores more (i.e., increases P_{2r}) and pulls the molecules closer together (i.e., increases the density ρ). This phenomena helps stabilize orientational LC ordering of the cores at higher T . As with the LJ nondipolar system, there is a subtle competition between energy and entropy effects in determining the relative stabilities of the S_A and N phases in the LJ dipolar system. (Figures 5 and 8 also show the average values of λ , P_{2f} , and P_{2i} as a function of T .)

For the relatively larger f_2 (i.e., $f_2 \geq 5$) in Figs. 2 and 3, the size of the T range of the high- T N phase in-

creases and the size of the T range of the S_A phases decrease as dipolar forces are added (in Fig. 3) to the LJ nondipolar system of Fig. 2. The dipolar forces orient the cores more, thus allowing the molecules to pack more efficiently in the N phase in the case with dipolar forces than in the case with no dipolar forces. While this effect is also seen in the S_A phases, the increase in packing efficiency is larger for $f_2 \geq 5$ in the N phase (with its positional disorder) than in the S_A phases [in which from the beginning, the cores are already oriented more (than in the N phase) due to the 1D positional alignment of oriented cores with other oriented cores].

For the relatively smaller f_2 (i.e., $f_2=4$) in Figs. 2 and 3, the increased orientation of the cores due to dipolar forces is more important in stabilizing the S_A phases at higher T and in stabilizing a low- T N phase. As T decreases, the tails stiffen somewhat, thus decreasing the packing differences between cores and tails. The need for segregated packing of cores with cores and tails with tails (as in a S_A phase) decreases and is overcome by the entropy of unsegregated packing, leading to a low- T N phase. Between $f_2=4$ and $f_2=5$ in Fig. 3, the conditions exist for this low- T N phase to become a reentrant N phase.

In summary, this paper has *predicted* and explained conditions for reentrant N phases in systems of molecules with two tail chains per molecule, with one tail at each end of the core. In this section of the discussion, we have seen how decreasing P , increasing E_g/k , and/or adding dipolar forces increases the frequency of occurrence of conditions for the existence of reentrant N phases in the systems studied in this paper. Subtle changes in these variables can make profound differences in the relative stabilities of the S_A and reentrant N phases.

Concluding Remarks

In passing, it is worth noting that the magnitudes of the relative density changes at the first-order transitions in the LJ nondipolar systems and LJ dipolar systems in this paper (see, for example, the ρ changes at the N - I transitions in Figs. 5, 7, and 8) are in good agreement with the range of experimental values (see, for example, Refs. 35–37). (See Ref. 1 for more illustration and discussion of this agreement for the LJ nondipolar system of Fig. 2.) Though not illustrated here, the relative entropy changes at the first-order transitions in the steric systems, the LJ nondipolar systems, and the LJ dipolar systems in this paper are in good agreement with the range of experimental values for these entropy changes. (See Ref. 1 for some illustration and for more discussion of this agreement for the LJ nondipolar system of Fig. 2.)

A second point to note in passing is that no multiply reentrant phases were seen in the particular systems studied in this paper, and also that preliminary studies using the theory of this paper for some other particular systems did not reveal multiply reentrant phases. [A multiply reentrant phase reappears more than one time as the temperature is lowered. Multiply reentrant S_A

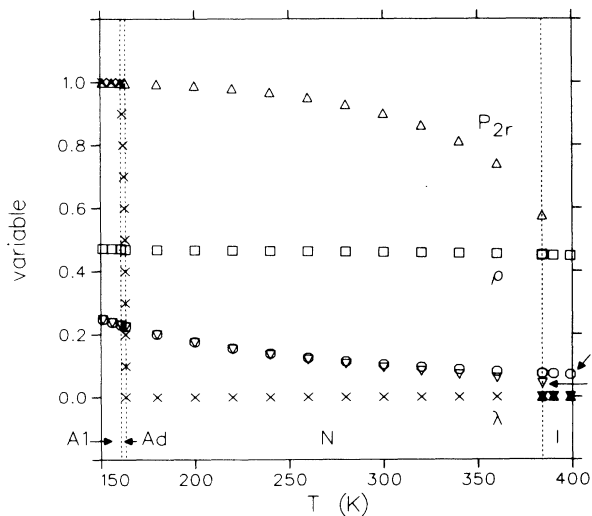


FIG. 8. Molecular ordering and thermodynamic variables λ , P_{2r} , P_{2f} , P_{2i} , and ρ as a function of temperature in different phases for $f_2=5$ for the LJ dipolar system calculated using the new approximate flexibility theory of this paper (and Ref. 1) with $E_g/k=250$ K. The dotted lines are defined as in Fig. 4, and the phase name abbreviations are as defined in Fig. 1.

and N phases are well established experimentally (see, for example, Refs. 17–18.)

In addition to the primary reasons (discussed in the “Introduction” section of this paper) for focusing in this paper (and in Ref. 1) on a new, better theory for the intrachain constraints on the tail-chain flexibility in LC molecules, a secondary reason was to look for possible multiply reentrant phases in the systems of this paper. In the old, more approximate theories for the tail-chain flexibility used in earlier papers,^{3–6} there were cases in which the chemical potentials of the S_A and N phases as a function of T approached each other rather closely and then diverged without actually crossing.³⁸ One question at that time was whether a more exact treatment of the flexibility would lead to the actual crossing of these chemical potential curves and thus perhaps multiply reentrant LC phases.³⁹

While no multiply reentrant phases were seen in the particular systems studied thus far with the theory of this paper here, it is possible that multiply reentrant phases could exist still in other, as-yet-unexplored systems that can be described by the theory of this paper for *intrachain* constraints on the tail-chain flexibility. In

another paper³³ to be published, new theories for the additional effect of *intermolecular* constraints on the tail-chain flexibility on reentrant and possible multiply reentrant LC phases are explored.

While this paper here deliberately deals with systems in which each molecule has two tail chains, the theory of this paper has also been extended³⁸ to systems in which each molecule has only one tail chain. In another paper⁴⁰ to be published, this new theory for one-tail molecules is applied to reentrant and possible multiply reentrant LC phases. Although multiply reentrant phases have thus far been seen experimentally (see, for example, Refs. 17 and 18) in systems in which each molecule has one tail chain and also has a large terminal dipole, we do not know if these two conditions are required for multiple reentrance or whether other molecular structures can also lead to multiple reentrance.

ACKNOWLEDGMENT

This research was supported by the U.S. Department of Energy.

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