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Intrachain flexibility constraints on phase stabilities and odd-even effects in multiple smectic-*A* and nematic liquid crystals

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The importance of the flexibility of *n*-alkyl tail chains in real liquid-crystal systems is reviewed. Two new microscopic, molecular statistical-physics theories (a full statistical theory and a simpler but accurate approximate theory) for the intrachain constraints on the *n*-alkyl tail-chain flexibility are presented and are compared with each other and with an old, more approximate theory for tail-chain flexibility used in earlier papers. The new approximate approach is computationally *much* faster than the full statistical method and is the first treatment to generate and explain odd-even effects in multiple smectic-*A* phases and the first treatment to generate and explain odd-even effects in smectic-*A* and nematic phases *without* resorting to *ad hoc* or arbitrarily adjustable fits to experimental data. Phase stabilities and odd-even effects for various thermodynamic and molecular ordering properties are calculated in the smectic-A_1, smectic-A_d, and nematic liquid-crystal phases and the isotropic liquid phase using the new approximate method. Some predictions and accompanying physical explanations are made for various systems that have not yet been chemically synthesized and/or experimentally studied. The theoretical results in this paper are in good semiquantitative and (in some cases) quantitative agreement with available experimental data and offer some *significant* improvements—compared with experiment—over the theoretical results of earlier papers, especially with regard to the relative stabilities of the nematic and multiple smectic-*A* phases. The calculations in this paper also show for the first time that intrachain constraints on the tail-chain flexibility are by far the major factor responsible for odd-even effects in these liquid-crystal systems.

I. 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. The general purpose of the theories 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.

LC's are formed by molecules with highly anisotropic shapes, with these shapes frequently changing as a function of temperature and density. From a basic viewpoint, the theoretical study of the *partial* orientational and positional ordering of such changing, highly anisotropic shapes in condensed phases is one of the most challenging problems in the statistical physics of many bodies.

From the standpoint of practical applications, LC ordering is the essential characteristic feature that determines the proper functioning of soaps and micelles (important in separation and extraction processes, such as enhanced oil recovery), LC polymers (important in their final solid state as stronger, lighter-weight replacements for metals in body armor, auto, and airplane parts, and other structural applications), LC display devices (important, for example, in digital watches and calculators, because of their small energy requirements), and biomembranes and other biological structures. LC structures are also found between crystalline and amorphous layers in "semicrystalline" polymers (the common state of a very large number of solid polymers), in coals and other fossil energy systems, etc.

In particular in this paper, we want to take a much closer, much more exact look at the effect of the molecule tail-chain flexibility on the stability of multiple smectic-*A* (Sm*A*) and nematic (*N*) LC phases than in previous papers.[1–4] More specifically, the purpose of this paper is to present and show results for two new methods (a full statistical method and a new rapid, but rather accurate approximate method) of describing the *intra*chain constraints on the flexibility of *n*-alkyl (hydrocarbon) tail chains in LC molecules and how these intrachain constraints affect odd-even alterations in the magnitudes of thermodynamic and molecular ordering properties (or in the increments between values of these properties) as the number of —CH_2— and —CH_3 groups in a given *n*-alkyl tail chain in a molecule varies from odd to even in these LC phases. These odd-even effects (while they do occur elsewhere) are especially noticeable at phase transitions.

An example of a reasonably typical LC molecule structure[5,6] is

$$H_3C\text{—}(CH_2)_y\text{—}[\text{—}O\text{—}\varnothing\text{—}N{=}N\text{—}\varnothing\text{—}O\text{—}]\text{—}(CH_2)_{y'}\text{—}CH_3$$

(∅ indicates a para-substituted benzene ring; $y,y' \sim 0-20$; y and y' may be equal or unequal.) The segment [· · ·] is the rigid core, on either side of which is a semiflexible n-alkyl tail chain. 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 SmA and N LC phases and the isotropic liquid (I) phase, there is essentially[7] free rotation of the molecule about the core long axis, thereby giving an effective rodlike, cylinderical shape to the core.[8,9]

The n-alkyl tail chains are partially flexible (semiflexible) since it costs a finite, but easily achievable, energy to make rotations about any carbon-carbon bond between —CH$_2$— (methylene) or —CH$_3$ (methyl) units in a given tail chain. There are three rotational energy minima for a given carbon-carbon bond in these tail chains: one *trans* rotational state and two *gauche* rotational states. The net energy difference between the *trans* state and either of the two *gauche* states is E_g, with the *gauche* states having the higher energy. The statistical distributions of *trans* and *gauche* rotational states as a function of E_g and the temperature are the origin of the *intra*chain constraints on the tail-chain flexibility.

It is emphasized that there is an appreciable fraction of *gauche* states 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, better methods of describing these intrachain constraints on the tail-chain flexibility is prompted by the following reasons. First, calculations[2–4] with a simple, rather approximate treatment of the tail-chain flexibility[1–4] have shown that the tail flexibility is important in understanding multiple SmA and reentrant-nematic LC phases.

In particular, Refs. 2 and 3 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 SmA [including[3] smectic-A_1 (SmA_1) and smectic-A_d (SmA_d)] and low-temperature N (including reentrant-N) LC phases. It is not necessary to invoke dipolar forces[4] (or even attractive forces[4] of any kind) to have these phases.

These theoretical results thus explained,[1–4] for the first time, the following experimental observations: With two or three exceptions,[6,10] virtually all molecules that form SmA—in fact, that form any kind of smectic (i.e., layered)—LC phases have one or more pendant semiflexible tail chains.[5,6,11] Furthermore, as the tail chains are shortened, the smectic phases disappear.[5,6,11]

In these experimental cases, the cores (and hence, any dipoles in the cores) are not sufficient (without the nonpolar 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.[1–4]

A second reason for focusing in this paper on new, better methods of describing intrachain constraints on the tail-chain flexibility in LC molecules is that there so far does not appear to have been a theoretical treatment for the odd-even effects in both SmA and N LC systems that generates and explains these effects without the less than satisfactory situation of having to resort at the very least to some "handwaving" and/or to some *ad hoc* or arbitrarily adjustable parameters (including arbitrary fits to experimental data). In fact, there so far does not appear to have been any theoretical treatment of odd-even effects in multiple SmA phases (SmA_1 and SmA_d phases).

Therefore, the new theory of this paper shows for the first time how the intrachain constraints on the flexibility of the tail chains can affect the odd-even alterations in thermodynamic and molecular ordering properties in the I phase and the N, SmA_1, and SmA_d LC phases formed by molecules composed of rigid rodlike cores and semiflexible tail chains. We note that in the theory of this paper (as in Ref. 4), the molecules can have the following intermolecular interactions between the different sites (chemical groups) in the different molecules: (1) site-site (segmental) hard (infinitely large) repulsions, (2) soft (finite) repulsions and London dispersion attractions using segmental Lennard-Jones (12-6) potentials, and (3) segmental dipolar interactions (dipole-dipole forces and dipole-induced dipole forces).

In the theory of this paper (as in Refs. 1–4), there are *no ad hoc* or arbitrarily adjustable parameters. 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. In this paper (as in Refs. 1–4), we do *not* use parameters to fit our calculated results to experimental LC data since such fitting would obfuscate (i.e., confuse) 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 and the odd-even alterations in these phases.

II. THEORY

A. General partition function

The new theoretical treatments for the intrachain constraints on the tail-chain flexibility in this paper can be best understood by first discussing in this subsection the overall setting (i.e., the general partition function) in which the intrachain constraints will eventually appear. (The in-depth derivation and explanation of the new theoretical treatments for these intrachain constraints can then be most logically and efficiently presented in Sec. II B.)

We begin with a localized[1–4] 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.[1,2] 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 —CH_2— group).

We use here a simple-cubic lattice theory. Each molecule has a total of m connected inpenetrable 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 then use combinatorial lattice statistics (after the manner of Refs. 1–4 and 12 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 theories of this paper (and of Refs. 1–4 and 12) 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.

The following five reasons give us 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 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) as well as in the lattice theories of Refs. 1–4 and 12, 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 as well as in the lattice theories of Refs. 1–4 and 12, 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. 1) used to derive the analytic partition function [Eq. (1) below] in this paper have been found to be *quite* accurate when compared with Monte Carlo computer simulations[13] in at least one limiting case presently amenable to such simulations. (See discussion in Ref. 1.)

(5) The lattice theories of Refs. 1–4 (and references therein)—which form the starting point for the new theories of this paper—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 very good agreement with existing and later experimental data. (See Refs. 1–4 and 12, as well as the review articles of Refs. 14 and 15 and references therein.)

The configurational partition function Q (derived from the combinatorial lattice statistics) in this paper is given (after the manner of Refs. 1–4) by

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

where Ω is the part of the partition function due to steric [hard (infinitely large)] repulsions between molecular segments (that is, one cannot lay two molecular segments on the same lattice site), E_I is the part of the partition function due to other intermolecular interactions [including soft (finite-sized) repulsions, London dispersion attractions, dipole-dipole interactions, and dipole-induced dipole interactions between molecular segments], k_B is the Boltzmann constant, and T is the absolute temperature.

In this paper (after the manner of Ref. 4) Ω and E_I (and thus Q) are functions of 16 basic molecular and thermodynamic variables. That is, to summarize in condensed mathematical notation,[4]

$$\Omega=\Omega(T,\rho,v_0,r,f_1,f_2,E_g,P_{2r},\lambda)$$

and

$$E_I=E_I(T,\rho,v_0,r,f_1,f_2,E_g,P_{2r},\lambda \ , \\ a_\sigma,\epsilon_{cc},\epsilon_{tt},\mu_{D\parallel},\mu_{D\perp},\alpha_c,\alpha_t) \ ,$$

where these molecular and thermodynamic variables 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); $0<\rho\le 1$. v_0 is the volume of one lattice site (i.e., hard-repulsive volume of one molecular segment). r is the number of rigid segments in a molecule. f_1 and f_2 are the number of semiflexible segments in tail chains 1 and 2, respectively, in a molecule. (The total number f of semiflexible segments in a molecule is given by $f=f_1+f_2$.) 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)]; $0\le P_{2r}\le 1$. λ is the average fraction[1–4] 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[1–4] 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 SmA 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.

In summary, P_{2r} and λ are the fundamental variables for the orientational (i.e., LC) order and the 1D positional (i.e., SmA) order, respectively, in the system. T, f_1, f_2, and E_g are the fundamental variables used to calculate the intrachain constraints on the tail-chain flexibility. Also, ρ, v_0, r, a_σ, ϵ_{cc}, ϵ_{tt}, $\mu_{D\parallel}$, $\mu_{D\perp}$, α_c, and α_t (together with P_{2r}, λ, T, f_1, f_2, and E_g) are the fundamental variables required to calculate the hard repulsions between molecular segments and the following other intermolecular site-site interactions [ω_{yz}'s, where y and z indicate either core (c) or tail (t) segments]: Lennard-Jones (12-6) potentials for soft repulsions and London dispersion attractions, dipole-dipole interactions, and dipole-induced dipole interactions.

Except for the changes noted in the remainder of Sec. II, Ω and E_I in the partition function of Eq. (1) in this paper are the same as Ω and E_I in Eqs. (2)–(13) of Ref. 4 and, due to space constraints, are not repeated in this paper. The symbols η and v in Ref. 4 have become the symbols P_{2r} and P_{2i}, respectively, in this paper.

P_{2i} is the average tail *intra*molecular orientational order (i.e., a measure of the average stiffness of the tails) where by analogy to P_{2r},

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

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

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

$$2u = \left[\sum_\gamma 2u_\gamma f_\gamma \right] \Big/ \left[\sum_\gamma f_\gamma \right] \ , \tag{3}$$

where f_γ is the number of semiflexible segments (—CH$_2$— or —CH$_3$ groups) in tail chain γ of the molecule, 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,

$$f = \sum_\gamma f_\gamma \ . \tag{4}$$

In Sec. II B, $2u_\gamma$ is determined by two different methods as a function of E_g, T, and f_γ.

B. Intrachain constraints on the tail flexibility in the partition function

This paper differs from earlier papers[1–4] in that the intrachain constraints on the tail-chain flexibility are treated in this paper by two much more sophisticated theoretical methods than the method used in the earlier papers. That is, $2u_\gamma$ and thus $2u$ in Eqs. (2) and (3) in this paper are calculated by better theoretical treatments than the treatment used in earlier papers.[1–4]

Specifically, $2u_\gamma$ in Eq. (3) is determined by two slightly different methods [Method 1: full statistical; and Method 2: new approximation (rapid, but rather accurate)] in this paper. With both methods, each semiflexible tail bond has three choices of direction, which mimic the three choices [*trans*, *gauche* (+), *gauche*(−)] of rotation (specifically, rotational energy minima) about the tetrahedrally coordinated carbon-carbon bonds between methylene (or methyl) groups in n-alkyl tail chains in LC molecules.

A *trans* tail-bond choice has a Boltzmann statistical weight of

$$\zeta_1 = 1/(1+2\Lambda) \ , \tag{5}$$

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

$$\zeta_2 = \Lambda/(1+2\Lambda) \ , \tag{6}$$

where

$$\Lambda = \exp[-E_g/(k_B T)] \ . \tag{7}$$

In both methods of calculating $2u_\gamma$ in this paper, the *trans-gauche* rotation choice of the first semiflexible tail bond next to the core is referenced with respect to the core long axis.

In both methods of calculating $2u_\gamma$, let state 1 be the state of a tail bond aligned parallel to the long axis of the core of the molecule. Let states 2 and 3 be the states in which the tail bond is bent out of the direction of the core long axis. (If state 1 is parallel to axis i of the system, then states 2 and 3 are parallel to axes j and k, respectively, of the system—where axes i, j, and k are orthogonal to each other in the simple-cubic lattice.) These states 1, 2, and 3 are achieved by various sequences of *trans* (t), *gauche* (+) (g^+), and *gauche*(−) (g^-) choices in the tail chain.

A sequence of bonds in a tail chain in which each bond is in state 1 corresponds to an all-*trans* sequence in the tail chain. For this 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 $g^{\pm}g^{\mp}$ are energetically very unfavorable[16,17] and therefore are not allowed[17] in this paper. [In a simple-cubic lattice, a sequence of $g^{\pm}g^{\mp}$ choices corresponds to a sequence of states iji (where $j \neq i$ and where i and j refer to states 1, 2, or 3).]

1. Method 1 (full statistical)

The rotation of a semiflexible bond in a tail chain is coupled to sequences of all preceding neighbors in that chain,

$$2u_{\gamma} = \left[\sum_{n=1}^{f_{\gamma}} 2u_n(f_{\gamma}) \right] \Big/ f_{\gamma} , \tag{8}$$

where $2u_n$ is the fractional probability that the semiflexible bond between molecular segment $(n-1)$ and semiflexible tail segment n is in state 2 or 3 [the semiflexible segments (or bonds) in a tail chain are numbered from 1 to f_{γ}, starting at the semiflexible tail segment (or bond) closest to the core and counting out to the end of the tail chain],

$$2u_n(f_{\gamma}) = X_{n1}(f_{\gamma})/X_{n2}(f_{\gamma}) , \tag{9}$$

where $X_{n1}(f_{\gamma})$ is the sum of the products of statistical weights for all allowed sequences of t, g^+, and g^- for all f_{γ} segments in the γ tail chain for which the bond between tail segment $(n-1)$ and tail segment n is in state 2 or 3. $X_{n2}(f_{\gamma})$ is the sum of the products of statistical weights for all allowed sequences of t, g^+, and g^- for all f_{γ} segments in the γ tail chain for which the bond between tail segment $(n-1)$ and tail segment n is in any one of the three states 1, 2, or 3.

In this paper $X_{n1}(f_{\gamma})$ and $X_{n2}(f_{\gamma})$ [and thus $2u_n(f_{\gamma})$] were calculated by the simple method of enumerating (on the computer) all the sequences of possible states 1, 2, and 3 for each semiflexible bond in the tail chain γ and then summing the products of the statistical weights of the appropriate sets of all allowed sequences of t, g^+, and g^- thus generated. The same values for $2u_n(f_{\gamma})$ can also be calculated using a simple-cubic analogue of the irreducible tensor method of Ref. 17 that was applied (in that reference) to orientational correlations *within* a semiflexible polymer chain. Both the full statistical method of this paper and the method of Ref. 17 seem to require about the same level of computational effort for the relatively short chains (i.e., 20 or fewer methylene groups per chain) in monomeric LC's, as in this paper here.

Both these calculational methods will give the same values for $2u_n(f_{\gamma})$ as the simple-cubic analogue of earlier approaches of enumerating[16,18,19] all allowed sequences of t, g^+, and g^- along a chain and *then* determining the direction of the vector of each tail bond down the chain relative to the core long axis. However, this third class of calculational methods is computationally much more intensive[17] than the method of this paper or the method of Ref. 17.

We note that the full statistical method in this paper here for calculating intrachain constraints on the tail-chain flexibility [i.e., for calculating $2u_{\gamma}$ in Eq. (3)] is completely accurate for the simple-cubic lattice, under the conditions (as outlined above) that (1) a statistically weighted average of all possible sequences of *trans* and *gauche* rotational states in the tail chain is used, and (2) sequences of the very energetically unfavorable $g^{\pm}g^{\mp}$ are not allowed. As the term "*intrachain* constraints" indicates, we are looking at properties of an isolated chain. As discussed above, these intrachain constraints are properties of E_g, T, and the chain length f_{γ}; and thus there are obviously *no* effects from neighboring chains (and thus, no assumptions of a mean field) in determining $2u_{\gamma}$ for a given tail chain. While there are no assumptions of a mean field in the determination of $2u_{\gamma}$ by the full statistical method of this paper, $2u_{\gamma}$ determined by this full statistical method could be inserted into the partition function of this paper for an entire system of molecules, and this partition function does assume localized mean fields. [As it turns out in this paper, we never do actually insert the $2u_{\gamma}$ determined by the full statistical method into the partition function. Rather (as discussed later) we use the full-statistical-method $2u_{\gamma}$ to check the new-approximate-method $2u_{\gamma}$, and then use the new-approximate-method $2u_{\gamma}$ in the partition function.]

2. Method 2 (new approximation)

For computational quickness with remarkable accuracy (see later), the rotation of a semiflexible bond in a tail chain is coupled to sequences of nearest, next-nearest, and next-next-nearest neighbors in the chain.

$$2u_{\gamma} = \left[\sum_{n=1}^{f_{\gamma}} 2u_n \right] \Big/ f_{\gamma} . \tag{10}$$

As in Eq. (8), n is the number of the position of the semiflexible tail segment (or bond) in a tail chain, where the tail segments (or bonds) are numbered from 1 to f_{γ}, starting at the tail segment (or bond) closest to the core and counting out to the end of the tail chain.

To summarize for $f_{\gamma}=1$,

$$2u_{\gamma} = 2u_1 = 2\zeta_2 . \tag{11}$$

To summarize for $f_{\gamma} \geq 2$, $2u_{\gamma}$ is determined from an initial dimer sequence (for even f_{γ}) or an initial trimer sequence (for odd f_{γ}) and then repeat dimer sequences (same for both even and odd f_{γ}) to make up the tail-chain length. The fractional probabilities $2u_n$ in the *initial* dimer and *initial* trimer sequences are coupled to the direction of the core long axis. The $2u_n$ probabilities in *any* dimer or trimer sequence are coupled to those probabilities in the *same* sequence and, as an approximation, are decoupled from those probabilities in *other* dimer or trimer sequences *in the tail.* (Dimers and trimers are the maximum lengths for which it is convenient to generate t, g^+, and g^- sequences analytically.)

That is, mathematically for $f_{\gamma} \geq 2$ in this new approximate method,

$$2u_\gamma=\left[\left[\sum_{j=1}^{2} Y_{1j}\right]+[(f_\gamma-2)/2]\left[\sum_{j=1}^{2} Y_{2j}\right]\right]\Big/ f_\gamma \qquad \text{even } f_\gamma\geq 2 \; ; \tag{12}$$

and

$$2u_\gamma=\left[\left[\sum_{j=1}^{3} Y_{3j}\right]+[(f_\gamma-3)/2]\left[\sum_{j=1}^{2} Y_{2j}\right]\right]\Big/ f_\gamma \qquad \text{odd } f_\gamma\geq 2 \; . \tag{13}$$

In the Y_{ij}'s above, the subscript $i=1$ refers to the initial dimer sequence of the tail (beginning at the core), $i=2$ refers to any repeat dimer sequence (dimer sequences after the initial dimer or initial trimer sequence), and $i=3$ refers to the initial trimer sequence of the tail (beginning at the core). In the Y_{ij}'s above, the subscript j refers to the position 1, 2, or 3 *in* the tail trimer (or the position 1 or 2 *in* the dimer), where one begins counting the position j from the end of the trimer (or dimer) that is closest to the core.

These Y_{ij}'s are given below, where the (respective) contributions (for each term) of the different sequences of *trans* (t), *gauche* (+) (g^+), and *gauche* (−) (g^-) are indicated:

$$Y_{11}=(2\zeta_1\zeta_2+2\zeta_2^2)/D_1 \; ; \tag{14a}$$

$$\{g^\pm t\},\{g^\pm g^\pm\} \; . \tag{14b}$$

$$D_1=\zeta_1^2+(2+2)\zeta_1\zeta_2+2\zeta_2^2 \; ; \tag{15a}$$

$$\{tt\},\{tg^\pm,g^\pm t\},\{g^\pm g^\pm\} \; . \tag{15b}$$

$$Y_{12}=[(2+2)\zeta_1\zeta_2+2\zeta_2^2]/D_1 \; ; \tag{16a}$$

$$\{tg^\pm,g^\pm t\},\{g^\pm g^\pm\} \; . \tag{16b}$$

$$Y_{21}=Y_{22}=[2\zeta_1^2+(4+2)\zeta_1\zeta_2+4\zeta_2^2]/D_2 \; ; \tag{17a}$$

$$\{tt\},\{tg^\pm,g^\pm t\},\{g^\pm g^\pm\} \; . \tag{17b}$$

$$D_2=3\zeta_1^2+(6+4)\zeta_1\zeta_2+6\zeta_2^2 \; ; \tag{18a}$$

$$\{tt\},\{tg^\pm,g^\pm t\},\{g^\pm g^\pm\} \; . \tag{18b}$$

$$Y_{31}=[2\zeta_1^2\zeta_2+(2+2+2)\zeta_1\zeta_2^2+2\zeta_2^3]/D_3 \; ; \tag{19a}$$

$$\{g^\pm tt\},\{g^\pm tg^\mp,g^\pm tg^\pm,g^\pm g^\pm t\},\{g^\pm g^\pm g^\pm\} \; . \tag{19b}$$

$$D_3=\zeta_1^3+(2+2+2)\zeta_1^2\zeta_2+(2+2+2+2)\zeta_1\zeta_2^2+2\zeta_2^3 \; ; \tag{20a}$$

$$\{ttt\},\{ttg^\pm,tg^\pm t,g^\pm tt\},\{tg^\pm g^\pm,g^\pm tg^\mp,g^\pm tg^\pm,g^\pm g^\pm t\},\{g^\pm g^\pm g^\pm\} \; . \tag{20b}$$

$$Y_{32}=[(2+2)\zeta_1^2\zeta_2+(2+2+2+2)\zeta_1\zeta_2^2+2\zeta_2^3]/D_3 \; ; \tag{21a}$$

$$\{tg^\pm t,g^\pm tt\},\{tg^\pm g^\pm,g^\pm tg^\mp,g^\pm tg^\pm,g^\pm g^\pm t\},\{g^\pm g^\pm g^\pm\} \; . \tag{21b}$$

$$Y_{33}=[(2+2+2)\zeta_1^2\zeta_2+(2+2+2)\zeta_1\zeta_2^2]/D_3 \; ; \tag{22a}$$

$$\{ttg^\pm,tg^\pm t,g^\pm tt\},\{tg^\pm g^\pm,g^\pm tg^\pm,g^\pm g^\pm t\} \; . \tag{22b}$$

Thus, for even $f_\gamma\geq 2$, $2u_1=Y_{11}$, $2u_2=Y_{12}$, and $2u_n(n\geq 3)=Y_{21}=Y_{22}$. For odd $f_\gamma\geq 2$, $2u_1=Y_{31}$, $2u_2=Y_{32}$, $2u_3=Y_{33}$, and $2u_n(n\geq 4)=Y_{21}=Y_{22}$.

The numerators of the Y_{ij}'s above are the analogues of the full-statistical-method X_{n1}'s [in Eq. (9)] for the initial dimer, initial trimer, and repeat dimer sequences, while the denominators D_i's in the Y_{ij}'s are the analogues of the full-statistical-method X_{n2}'s [see Eq. (9)] for these trimer and dimer sequences. Clearly, for $f_\gamma\leq 3$, the full-statistical-method and this new-approximate-method are exactly the same.

A *major conclusion,* as seen in Figs. 1(a)–1(c) for some $f_\gamma\geq 4$, is that this new approximate method for calculating $2u_\gamma$ (as a function of f_γ) is found to be remarkably accurate compared with the full statistical method. Plus, the new approximate method is computationally *much* faster than the full statistical method.

[We also note that a slight odd-even effect in $2u_n$ as a function of n and f_γ is generated[20(a)] when $2u_n$ is calculated by the full statistical method of Eq. (9) for the simple-cubic lattice. With the computational approximation of using trimer and dimer sequences as discussed above, the new approximate method here for the simple-cubic lattice emphasizes this odd-even effect in $2u_n$ (and thus, in $2u_\gamma$) even more, as one might expect these odd-even effects to be emphasized more in the tetrahedral coordination of real n-alkyl chains attached to a rigid rodlike core. Yet, this increased emphasis in the new approximate method is small enough that there is still very good agreement in $2u_\gamma$ (see Fig. 1) between the full statistical method and the new approximate method on the simple-cubic lattice, and thus we have confidence that the new approximate method is still consistent with the other parts of the partition function of Eq. (1) derived for the simple-cubic lattice. So, the new approximate method would appear to be a very reasonable compromise between (1) the full statistical method for the simple-cubic lattice (recalling that this lattice is used for mathematical tractability), and (2) n-alkyl chains in real LC molecules.]

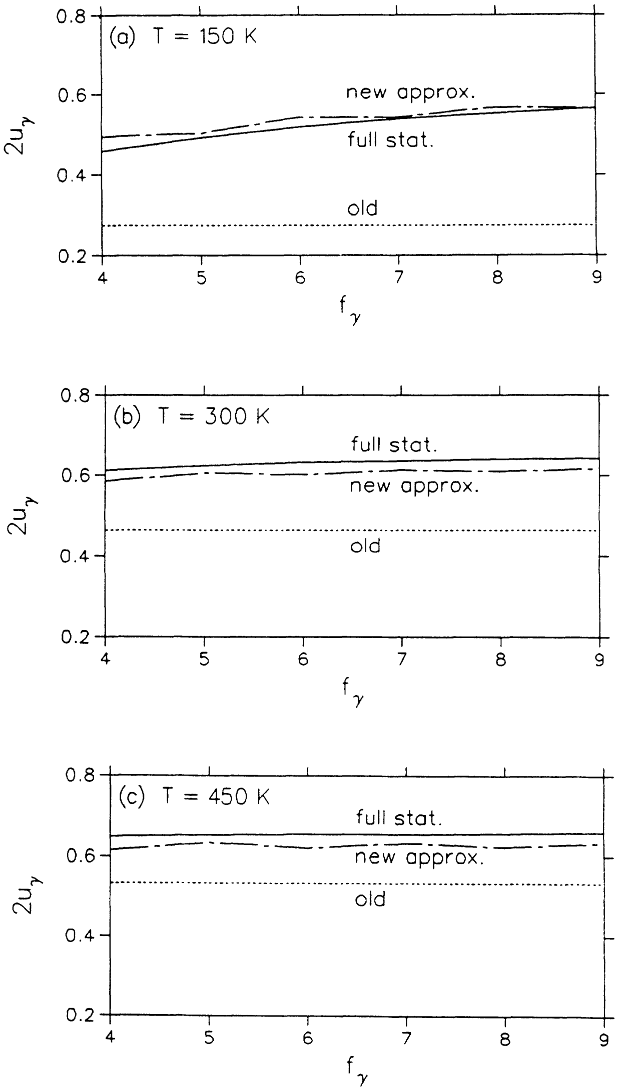

FIG. 1. Average fraction $2u_\gamma$ of semiflexible bonds in tail chain γ bent out of the direction of the long axis of the core of the molecule vs the number of f_γ of segments in tail chain γ for the full statistical method of this paper, for the new approximate method of this paper, and for the old method of Refs. 1–4 for the following temperatures T: (a) $T=150$ K, (b) $T=300$ K, and (c) $T=450$ K. The lines (solid, dotted, and dash-dotted) connect the values of $2u_\gamma$) calculated for integer values of f_γ and have been drawn to aid the eye in observing any odd-even effects.

C. Using the partition function in this paper

Various thermodynamic equations are obtained (after the manner of Refs. 2 and 12) from the partition function Q, including (1) a pressure-volume-temperature (P-V-T) 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 practice in two cases,[20(b)] 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.

When T is an unknown when iterating with the above three equations, the full statistical method of calculating $2u_\gamma$ in Eq. (8) is much too intensive computationally. Furthermore, while it appears possible in principle to iterate to a stable solution *using the full statistical method* with T as an unknown in these equations, in practice these interactions using the full statistical method have not converged[20] in a reasonable period of time. Therefore in this paper *all* phase diagrams were calculated using the new approximate method of calculating $2u_\gamma$, rather than the full statistical method.

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 SmA phases. $\lambda=0$ in the I and N phases.

The 1D positional alignment of the centers of mass (and thus, of the rigid cores) of the oriented molecules is the basis of SmA layers. This actual positional alignment (i.e., segregrated packing) of cores with cores (and thus, of tails with tails) for oriented molecules in this theory results in a core-rich region and tail-rich regions 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 SmA phase of some kind exists for any value of λ for which $0<\lambda\leq 1$.

The SmA_1 and SmA_d phases are physically defined[21] by the following relations between the layer thickness L and the molecules length d_L. $L=d_L$ in the SmA_1 phase, and $d_L<L<2d_L$ in the SmA_d phase.

Physically,[3] the only way to have a SmA_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 SmA_1 phase. The only way to have a SmA_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 SmA_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 *dis*alignment and hence the average fraction of the length of a given molecule that is out of register with its neighbors in the SmA plane.[2–4] Therefore, the layer thickness L in this paper is given by

$$L=d_L+(1-\lambda)d_L=(2-\lambda)d_L\ , \tag{23}$$

$$d_L = v_0^{1/3}\{r + f[(1+2P_{2i})/3]\} + (a - v_0^{1/3}) \ . \qquad (24)$$

In contrast to earlier papers,[2–4] d_L and thus L in 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 SmA_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 these earlier papers are unchanged, since they were all actually calculated using the basic variable λ, rather than the derivative variables L and d_L.)

Now we discuss how the other variables used in this paper are taken from experimental data for small chemical groups or are calculated in the theory. The site-site intermolecular interactions are calculated after the manner of Ref. 4.

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. $\omega_{ct\parallel} = \omega_{ct\perp} = \omega_{ct}$; and $\omega_{tt\parallel} = \omega_{tt\perp} = \omega_{tt}$. As in Ref. 4,

$$\omega_{yz} = \sum_{j=1}^{3} \omega_{yzj} \ , \qquad (25)$$

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. [In this paper as in earlier papers,[4,12] we have summed pair interactions over both empty and filled lattice sites (out to the first intermolecular neighbors), with interactions involving empty sites being assigned an energy of zero.]

As in Ref. 4,

$$\omega_{yz1} = 4\epsilon_{yz}[(a_\sigma/a)^{12} - (a_\sigma/a)^6] \ . \qquad (26)$$

$\omega_{cc1\parallel} = \omega_{cc1\perp}$. Here, $\epsilon_{cc}/k = 300$ K and $\epsilon_{tt}/k = 150$ K. These values are appropriate for benzene and methane molecules,[22(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 (as in Ref. 4), $a_\sigma = 4 \times 10^{-8}$ cm, an approximate average value appropriate for a methane or benzene molecule.[22(a)] a is the average separation distance between the centers of two first-neighbor intermolecular segments and is calculated here (as in Ref. 4) from ρ using

$$\rho = mv_0/v, \quad v = a^2[2a + v_0^{1/3}(m-2)] \ , \qquad (27)$$

where v is the average volume associated with one molecule, and $v_0 = 2.98 \times 10^{-23}$ cm^3, as estimated[3] from experimental measurements of various quantities.

ω_{yz2} and ω_{yz3} are calculated (after the manner of Ref. 4) using Eqs. (13.5-3) and (1.3-8), respectively, of Ref. 22(b) using values of $\mu_{D\parallel}$, $\mu_{D\perp}$, α_c, and α_t estimated from experimental bond and group dipole moments[23(a),24] and polarizabilities.[23(b)] Here, $\alpha_t = 2 \times 10^{-24}$ cm^3, a value appropriate for a methylene group. For a core with relatively large dipolar forces, of the order of those in a cyanobiphenyl-oxy-type core, appropriate values[4] for $\mu_{D\parallel}$ and α_c are $\mu_{D\parallel} = 5.2D$ and $\alpha_c' = \alpha_c(r-2) = 24 \times 10^{-24}$ cm^3; $(r-2)$ is the number of rigid segments having core-type interactions.[4,12]

After the manner of Ref. 4; also,

$$\omega_{cc2\parallel} = \omega_{cc2\perp} = -(\mu_{D\parallel}^2 + \mu_{D\perp}^2)\alpha_c/[a^6(r-2)^2] \ , \qquad (28)$$

and

$$\omega_{ct2} = -(\mu_{D\parallel}^2 + \mu_{D\perp}^2)\alpha_t/[2a^6(r-2)^2] \ . \qquad (29)$$

Also,

$$\omega_{cc3\parallel} = -\mu_{D\parallel}^2/\{2[a(r-2)]^3(1+\chi q\lambda)\} \ , \qquad (30)$$

where $\chi = 1$ for $\omega_{cc3\parallel}$ in Eq. (7) in Ref. 4, and $\chi = 0$ for $\omega_{cc3\parallel}$ in Eq. (12) in Ref. 4; also,

$$\omega_{cc3\perp} = -\mu_{D\perp}^2/\{2[a(r-2)]^3\} \ . \qquad (31)$$

Also (as in Ref. 4), $\omega_{tt2} = \omega_{ct3} = \omega_{tt3} = 0$.

If $\mu_{D\perp} = 0$ (as in Ref. 4 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 (as in Ref. 4), $r = 4$, as estimated[8(a),25] from experimental data for typical length-to-breadth ratios of the rigid cores of real LC molecules. Also, $E_g/k = 250$ K as estimated[16] from experimental data for the *trans-gauche* energy difference in typical n-alkyl chains.

III. RESULTS AND DISCUSSION

A. Intrachain contributions to the flexibility

Figures 1(a)–1(c) show plots of $2u_\gamma$ [the average fraction of semiflexible bonds in tail chain γ bent out of the direction of the long axis of the core of the molecule (or equivalently, bent out of the direction of the long axis of the all-*trans* state of the tail chain of the molecule)] versus the tail-chain length f_γ. These results were calculated using (1) the full statistical method of this paper, (2) the remarkably accurate new approximate method of this paper, and (3) the old, rather more approximate method of Refs. 1–4.

In the old method of Refs. 1–4,

$$2u_\gamma = 2u_n = 2\zeta_2 \qquad (32)$$

for all values of f_γ and n. Thus in this old method, the rotation of a semiflexible bond is coupled directly to the direction of the long axis of the core of the molecule. Consequently, since a *gauche* energy is assigned for each bond rotated out of the direction of the core long axis, the old method includes in a rather approximate manner some *inter*molecular constraints on the intramolecular *trans-gauche* flexibility. That is, the old method reflects in a rather approximate manner that it should be harder (i.e., cost more net energy) to make a rotation out of the core long axis since such a rotated bond would run into more interference packing with the cores of neighboring molecules.

While the full statistical method and the new approximate method illustrated in Fig. 1 in this paper deliberately deal specifically with only intrachain constraints on the tail-chain flexibility, results calculated with the old method are included for general purposes of completeness and informal comparison. (In passing, it should be noted that $2u_\gamma = 2u_n = 2\zeta_2$ in all three methods for $\gamma = n = 1$.)

We note in Fig. 1 that as T increases, the results from the old method move closer to the results from the full statistical method and from the new approximate method. As T increases, the fraction of *gauche* states increases [see Eqs. (6) and (7)], and the approximation in the old method [see Eq. (32)] becomes more accurate.

B. Intrachain contributions to phase stabilities and odd-even effects

Figures 2–9 illustrate odd-even alternations in the magnitudes of various thermodynamic and molecular ordering properties (or in increments between values of these properties) as the number of —CH_2— or —CH_3 units varies from odd to even in tail chain 2 (i.e., as f_2 varies from odd to even) for a system of molecules having Lennard-Jones intermolecular interactions but *no* dipolar forces (i.e., all $\omega_{yz2} = \omega_{yz3} = 0$) studied using the new approximate method for intrachain constraints. We deliberately choose a system with no dipolar forces in order to emphasize that dipolar forces are not necessary for odd-even effects. In Figs. 2–9, $f_1 = 4$, and $P = 1$ atm.

Figure 2 illustrates odd-even effects in the temperatures at the transitions between the nematic (N), smectic A_d (SmA_d), and the smectic-A_1 (SmA_1) LC phases and the isotropic (I) liquid phase. In the particular calculations whose results are shown in the figures of this paper, the SmA_1-SmA_d and SmA_d-N transitions were found to be second order, and the N-I transitions were found to be weakly first order.

Two *major new conclusions* in this paper are as follows.

(1) The N phase is somewhat more stable with respect to the SmA phases (particularly at higher temperatures) in the Lennard-Jones nondipolar system when we use the new approximate method for the tail-chain flexibility in this paper (see Fig. 2) than when we used the old approximate method of earlier papers[1–4] (see Fig. 2 of Ref. 4). The improved stability of the N phase with respect to the SmA phases in this paper here is in *significantly better* general agreement with experiment (see, for example, Refs. 5, 6, and 11) than are the results of earlier papers.[2–4]

(2) We also note that while odd-even effects are *not* produced by the old method of Refs. 1–4, odd-even effects are observed experimentally (see, for example, Refs. 5, 6, and 11) and are produced by the new approximate method of this paper here. Thus, the new approximate theoretical treatment of intrachain constraints on the tail-chain flexibility in this paper offers a *significant improvement* (over the more approximate treatment of earlier papers[1–4]) in treating odd-even effects and phase stabilities in N, SmA_d, and SmA_1 LC phases and the I liquid phase.

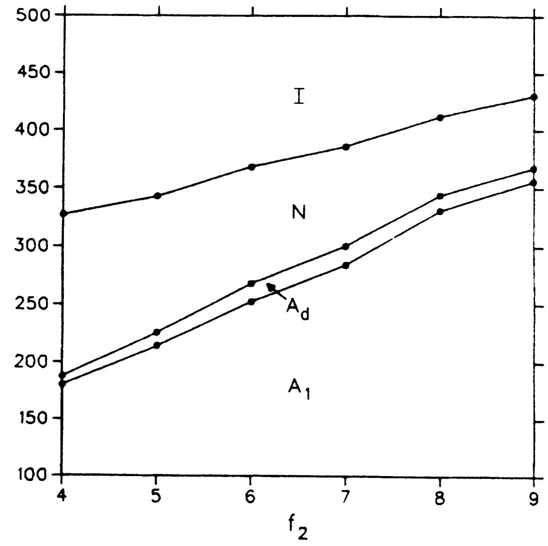

FIG. 2. Phase transition temperatures T (indicated by dots) vs the number f_2 of segments in tail chain 2 for the Lennard-Jones nondipolar system. The phase names are abbreviated as isotropic (I), nematic (N), smectic-A_1 (A_1), and smectic-A_d (A_d). The solid lines connect the dots and have been drawn to aid the eye in observing odd-even effects.

Figures 3–6 and 8 and 9 illustrate odd-even effects in the temperature T, average core orientational order P_{2r}

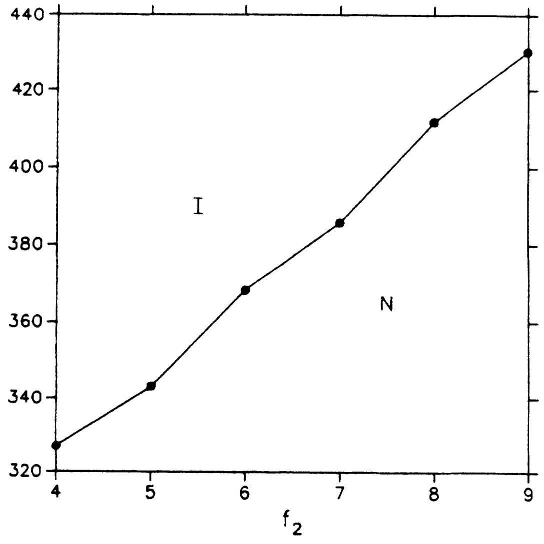

FIG. 3. Phase transition temperatures T (indicated by dots) vs the number f_2 of segments in tail chain 2 for the Lennard-Jones nondipolar system at the N-I transition. The solid lines are defined as in Fig. 2.

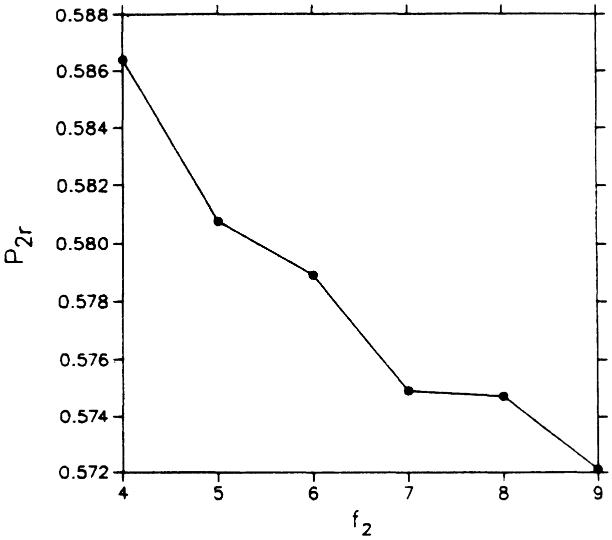

FIG. 4. Average core orientational order P_{2r} (indicated by dots) for the system vs the number f_2 of segments in tail chain 2 for the Lennard-Jones nondipolar system in the N phase at the N-I transition. The solid lines are defined as in Fig. 2.

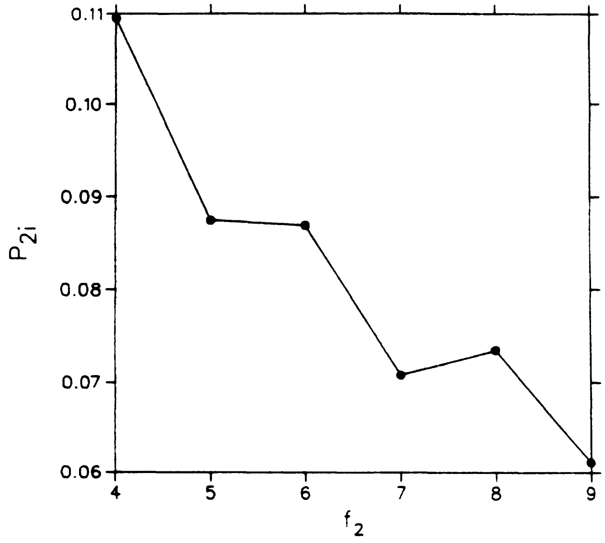

FIG. 6. Average tail *intrachain* orientational order P_{2i} (indicated by dots) for the system vs the number f_2 of segments in tail chain 2 for the Lennard-Jones nondipolar system at the N-I transition. The solid lines are defined as in Fig. 2.

for the system, average tail *inter*molecular orientational order P_{2f} for the system, average tail *intra*molecular orientational order (i.e., tail stiffness) P_{2i} for the system, relative density change $[10^2(\Delta\rho/\rho_N)]$ and reduced entropy change $[\Delta S/(N_m k_B)]$, respectively, at the N-I transition. The values for P_{2r} and P_{2f} shown in Figs. 4 and 5, respectively, are the values in the N phase at the N-I transition. It has been shown[2–4] that P_{2f} is given by

$$P_{2f}=P_{2r}P_{2i} \ . \tag{33}$$

Figure 7 illustrates odd-even effects in the average density ρ (i.e., fraction of lattice sites occupied by molecular segments) at the SmA_d-N transition. [While odd-even effects in P_{2r}, P_{2f}, P_{2i}, and ρ have been calculated[20(a)] for all three transitions (N-I, SmA_d-N, and SmA_1-SmA_d for the nondipolar system of this paper, Figs. 3–9 illustrate some of the more dramatic examples of these calculated results.]

While the very simple Lennard-Jones nondipolar system deliberately chosen (see earlier discussion) for study in this paper has not yet been synthesized, a comparison of the magnitudes of the transition T in Figs. 2 and 3

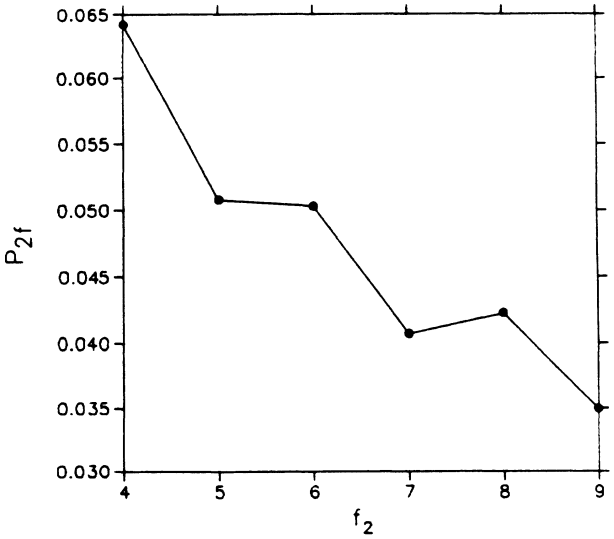

FIG. 5. Average tail *intermolecular* orientational order P_{2f} (indicated by dots) for the system vs the number f_2 of segments in tail chain 2 for the Lennard-Jones nondipolar system in the N phase at the N-I transition. The solid lines are defined as in Fig. 2.

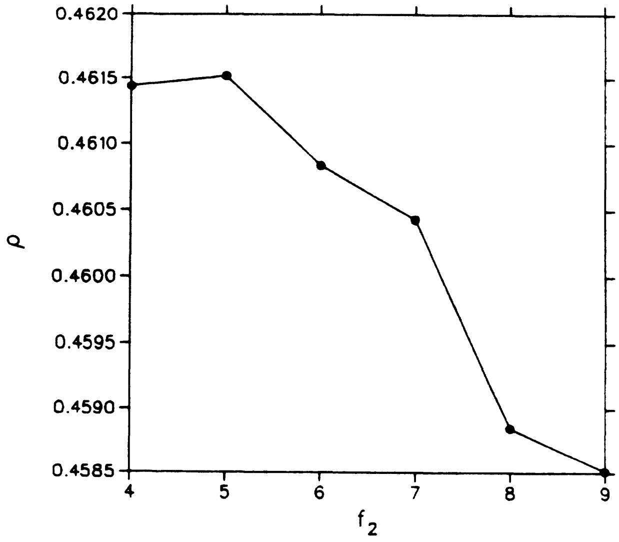

FIG. 7. Average density ρ (indicated by dots) vs the number f_2 of segments in tail chain 2 for the Lennard-Jones nondipolar system at the SmA_d-N transition. (ρ is the fraction of lattice sites occupied by molecular segments.) The solid lines are defined as in Fig. 2.

with the magnitudes of transition T for existing LC systems[5,6,11] with various specific molecule-chemical structures indicates that the transition T in Figs. 2 and 3 can be expected to be rather accurate from a semiquantitative viewpoint (and probably also from a quantitative viewpoint). The *major* contribution to the quantitative and semiquantitative values of the transition T at $P=1$ atm in this paper comes from the relatively realistic treatment of site-site intermolecular interactions (especially Lennard-Jones potentials for soft repulsions and attractions) very much after the manner of Refs. 4 and 12. (See also those two references for a comparison of calculated and experimental values for various thermodynamic and molecular ordering properties for different existing LC systems.)

We note that the odd-even effect in P_{2f} in Fig. 5 is larger than the odd-even effect in P_{2r} in Fig. 4, since the alternation of the number of —CH_2— units (or, carbon atoms) in the semiflexible n-alkyl tail chain itself is the origin of the odd-even effects. We do see some odd-even effects in P_{2r} because the cores and tails are attached to each other in the molecules, and thus the tails affect the cores.

We also note that the values of P_{2r} in Fig. 4 are about an order of magnitude larger than the values of P_{2f} in Fig. 5, since it is easier to orient rigid cores than semiflexible tail chains. We do see some ordering of the semiflexible tail chains because the cores and tails are attached to each other in the molecules, and thus the ordering of the cores affects the ordering of the tails.

The magnitudes of the relative density changes in Fig. 8 are in good agreement with experimental values (see, for example, Refs. 26–28). Also, the magnitudes of the reduced entropy changes in Fig. 9 are also in good agreement with experimental values [see, for example, Refs. 5, 11(a), and 29–38].

In Figs. 2–6 and 8, curves drawn through the values for the various thermodynamic and molecular ordering properties 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 in Figs. 7 and 9. Both cases ("evens high" and "odds high") for various physical properties are seen experimentally (see, for example, Refs. 5, 6, 11, and 18) in the same system and in different systems.

Another *major conclusion* of this paper is as follows. The magnitudes of the odd-even effects due to the *intrachain* constraints on the tail-chain flexibility in this paper appear, in general, to be almost as large as the magnitudes of the odd-even effects from experimental measurements in LC systems (see, for example, Refs. 5, 6, 11, and 18). This result implies that the intrachain constraints are by far the major factor responsible for odd-even effects in these systems and thus account for most of the magnitude of these odd-even effects.

In addition, the fact that the odd-even effects from intrachain constraints in this paper are a little smaller than the odd-even effects from experimental measurements indicates that *intermolecular* constraints on the tail-chain flexibility also make some contribution to the odd-even effects seen experimentally. However, the purpose of this paper here is to isolate and focus on contributions from intrachain constraints. In another paper[39] 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.

While we have noted good quantitative and semiquantitative agreement between calculated results and experimental results in general in this paper here, the *major*

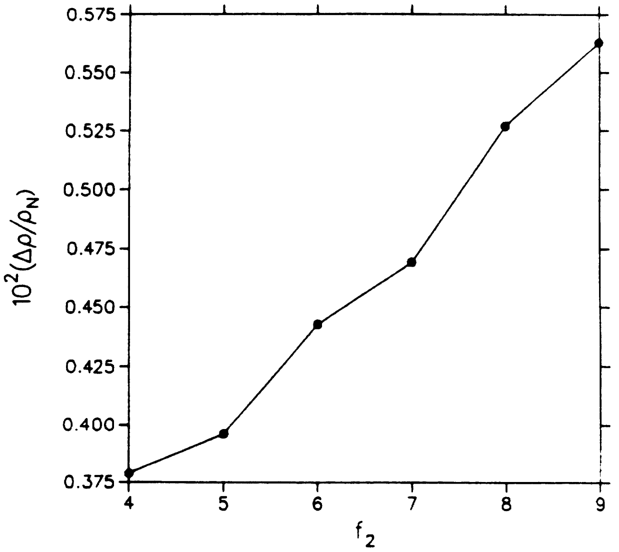

FIG. 8. Relative density changes $[10^2(\Delta\rho/\rho_N)]$ (indicated by dots) vs the number f_2 of segments in tail chain 2 for the Lennard-Jones nondipolar system at the N-I transition. [Note that $(\Delta\rho/\rho_N)$ has been multiplied by 100 before being plotted; ρ_N is the density in the N phase at this transition.] The solid lines are defined as in Fig. 2.

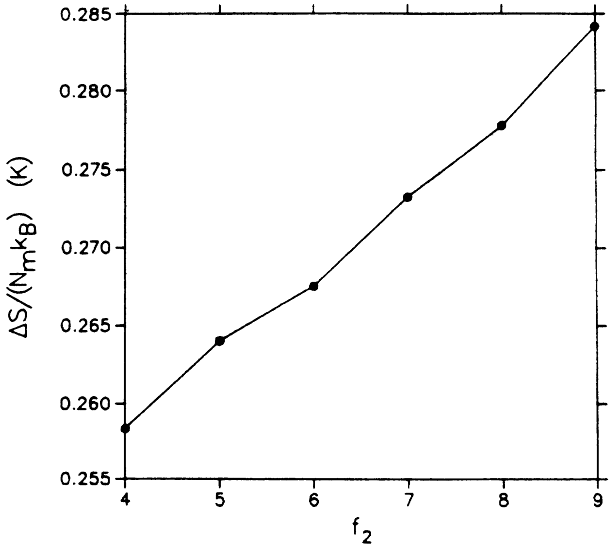

FIG. 9. Reduced entropy changes $[\Delta S/(N_m k_B)]$ (indicated by dots) vs the number f_2 of segments in tail chain 2 for the Lennard-Jones nondipolar system at the N-I transition. The solid lines are defined as in Fig. 2.

purpose of this paper here has been to *predict* and explain *trends* in thermodynamic and molecular ordering properties (including odd-even effects) as a function of pressure, temperature, and details of molecule chemical structure (including intrachain constraints on tail-chain flexibility). An exhaustive comparison of results calculated using the theory of this paper with experimental results for a large number of existing LC systems is properly left for later papers.

IV. CONCLUDING REMARKS

In conclusion, the importance of the flexibility of *n*-alkyl tail chains in real liquid-crystal systems was reviewed. Two new microscopic, molecular statistical-physics theories (a full statistical theory and a simpler, but accurate approximate theory) for the intrachain constraints on the *n*-alkyl tail-chain flexibility were presented and were compared with each other and with an old, more approximate theory for tail-chain flexibility used in earlier papers. The new approximate approach is computationally *much* faster than the full statistical method.

The new approximate method of this paper is the *first* treatment to generate and explain odd-even effects in *multiple* smectic-A phases and the first treatment to generate and explain odd-even effects in smectic-A and nematic phases *without* using *ad hoc* or arbitrarily adjustable parameters and *without* resorting to arbitrary fits to experimental data.

Phase stabilities and odd-even effects for various thermodynamic and molecular ordering properties were calculated in the smectic-A_1, smectic-A_d, and nematic liquid-crystal phases and the isotropic liquid phase using the new approximate method for intrachain contributions to the tail-chain flexibility. As discussed earlier in Sec. III the calculations in this paper are in good semiquantitative and (in some cases) quantitative agreement with available experimental data. Also, predictions and accompanying physical explanations are made for various systems that have not yet been chemically synthesized and/or experimentally studied.

The theoretical results with the new approximate method in this paper offer some *significant* improvements—compared with experiment—over the theoretical results of earlier papers. For example, the relative stabilities of the smectic-A phases with respect to the nematic phase are in better agreement with experiment when these stabilities are calculated using the new approximate theory of this paper.

The calculations in this paper show for the first time that intrachain constraints (as opposed to intermolecular constraints) on the tail-chain flexibility are by far the major factor responsible for odd-even effects in these liquid-crystal systems and thus account for most of the magnitude (size) of these odd-even effects.

In another paper[40] the new theories of intrachain constraints on the tail-chain flexibility in this paper here are applied to the problem of re-entrant and multiply-reentrant LC phases. [A reentrant phase is a phase that appears in one temperature range, disappears in a lower temperature range, and then reenters or reappears in an even lower temperature range. A multiply-reentrant phase reappears more than one time as the temperature is lowered. These reentrant and multiply-reentrant LC phases are well established experimentally (see, for example, Refs. 21 and 41 and references therein).]

In other papers[42] the new theories of this paper here are extended to treat liquid-crystal polymers (LCP's). Those papers treat both backbone LCP's and side-chain LCP's, as well as binary mixtures of a backbone LCP and a second component (which can be LC or non-LC, or polymeric or nonpolymeric).

Note added in proof. These theories for LCP's have also been used by this author[43] to predict and design (atom by atom, bond by bond) the first superstrong LCP's, several of which are now being chemically synthesized[44] at Los Alamos.

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