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TITLE NEW THEORY FOR COMPETING INTERACTIONS AND MICROSTRUCTURES
IN PARTIALLY-ORDERED (LIQUID CRYSTALLINE) PHASES

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New Theory for Competing Interactions and Microstructures in Partially-Ordered (Liquid-Crystalline) Phases

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1. SUMMARY

A summary of results from a unique statistical-physics theory to predict and explain competing interactions and resulting microstructures in some partially-ordered [in this case, liquid-crystalline (LC)] phases is presented. The static aspects of both partial orientational and partial positional ordering of the molecules into various microstructures in these phases (including the incommensurate smectic-Ad phase) can be understood in terms of various competing interactions (both entropic and energetic) involved in the packing together of the different molecular sub-units at given pressures and temperatures. These microstructures are predicted and explained (using no ad hoc or arbitrarily adjustable parameters) as a function of molecule chemical structure [including lengths and shapes (from bond lengths and angles), intramolecular rotations, site-site polarizabilities and pair potentials, dipole moments, etc.]. Theoretical results are presented for the nematic, re-entrant nematic, smectic-Ad, and smectic-A1 LC phases and the isotropic liquid phase.

2. INTRODUCTION

Liquid-crystalline (LC) phases are stable condensed phases in which the molecules pack together with order that is intermediate between the three-dimensional order of a crystalline solid and the disorder of an isotropic (ordinary) liquid. LC phases always have partial orientational order of the molecules, and some LC phases also have partial positional order of the molecules.

The partial molecular ordering that is characteristic of LCs occurs frequently in natural and synthetic materials. Thus, LCs are of considerable basic and applied interest [1].

LCs are formed by molecules with very anisotropic shapes (typically, with length-to-breadth ratios of three or more), 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 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 electro-optic devices (such as 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.

There are thousands of possible chemical structures in LCs. A reasonably typical example of a LC molecule structure is

(ϕ indicates a para-substituted benzene ring. $y, y' \sim 0$ to 20. y and y' may be equal or unequal.)

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 isotropic (I) liquid phase and in the particular LC phases studied in this paper, there is essentially free rotation of the molecule about the core long axis, thereby giving an effective rodlike, cylindrical shape to the core.

The n-alkyl tail-chains are partially-flexible (semiflexible) since there are one trans and two gauche rotational energy minima for a carbon-carbon bond between methylene ($-\text{CH}_2-$) or methyl ($-\text{CH}_3$) units in a given chain section. There is an appreciable fraction of gauche states (the higher energy states) in n-alkyl tail-chains in LC and I phases. In this paper, each molecule has two tail-chains.

3. THEORY

In the theory of this paper, the chemical structure of each molecule is divided into a sequence of connected sites, where these sites correspond to small groups of atoms (such as benzene rings and methylene groups). We then use a localized mean-field (LMF) simple-cubic (SC) lattice theory to study the packing of the molecules in the system volume.

We use SC lattice theory since any orientation of a molecule or molecular part or bond can be decomposed into its x , y , and z components and mapped directly onto a SC lattice in a manner analogous to normal coordinate analysis; in, for example, molecular spectroscopy. LMF means that there is 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. These local regions are determined by the actual packing of the molecules in the system. This packing is done mathematically using lattice combinatorial statistics to determine the analytic partition function for the system. [The generalized combinatorics used in the theory of this paper have been found to be quite accurate when compared with Monte Carlo computer simulations[2] in at least one limiting case presently amenable to such simulations (see discussion in Ref. 3)]. Various continuum limits are taken in the theory of this paper.

The partition function and the resulting equations for static thermodynamic and molecular ordering properties are functions of the pressure P , temperature T , density ρ , lengths and shapes of the rigid core and the semiflexible tail-chains of a molecule, net energy difference E_g between trans and gauche states, dipole moments, site-site polarizabilities and Lennard-Jones (12,6) potentials, degree of polymerization, and orientational and one-dimensional (smectic-A) positional orderings of the different rigid and semiflexible parts of the molecules. The Lennard-Jones (LJ) potentials are used to calculate repulsions and London dispersion attractions between different molecular sites and the dipole moments and polarizabilities are used to calculate dipole/dipole and dipole/induced dipole interactions between different molecular sites.

There are no ad hoc or arbitrarily adjustable parameters in this theory. All variables used in this theory are taken from experimental data for atoms or small groups of atoms or are calculated in the theory.

The theory used in this paper has been derived in detail elsewhere [4] and involves extension and refinement of earlier, very successful theories [3,5-7] for LCs. Due to length constraints on this paper, we note only the changes made in this paper to the equations of Refs. 3 and 5-7.

The equations in the theory of this paper are the same as the equations of Ref. 7, except for the following changes (Variables not defined in this paper have been previously defined in Ref. 7.)

The treatment of the flexibility of a semiflexible tail-chain in Ref. 7 was significantly refined in Ref. 4. Thus, Eq. (14) of Ref. 7 is replaced in this paper by

$\nu = \langle (3 \cos^2 \psi - 1) \rangle / 2 = 1 - 3u$, where f_γ is the number of semiflexible segments ($-\text{CH}_2-$ or $-\text{CH}_3$ groups) in tail-chain γ of the molecule,

$$2u = (\sum_\gamma 2u_\gamma f_\gamma) / (\sum_\gamma f_\gamma), \quad f = \sum_\gamma f_\gamma, \quad 2u_\gamma = 2\zeta_\gamma \text{ for } f_\gamma = 1,$$

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

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

$$Y_{11} = 2(\zeta_1 \zeta_2 + \zeta_2^2) / D_1, \quad Y_{12} = 2(\zeta_1^2 \zeta_2 + \zeta_2^2) / D_1,$$

$$Y_{21} = Y_{22} = 2(\zeta_1^2 + 3\zeta_1 \zeta_2 + 2\zeta_2^2) / D_2, \quad Y_{31} = 2(\zeta_1^2 \zeta_2 + 3\zeta_1 \zeta_2^2 + \zeta_2^3) / D_3,$$

$$Y_{32} = 2(2\zeta_1^2 \zeta_2 + 4\zeta_1 \zeta_2^2 + \zeta_2^3) / D_3, \quad Y_{33} = 6(\zeta_1^2 \zeta_2 + \zeta_1 \zeta_2^2) / D_3,$$

$$D_1 = \zeta_1^2 + 4\zeta_1 \zeta_2 + 2\zeta_2^2, \quad D_2 = 3\zeta_1^2 + 2(5\zeta_1 \zeta_2 + 3\zeta_2^2),$$

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

$$\zeta_1 = 1/(1 + 2\Lambda), \quad \zeta_2 = \Lambda/(1 + 2\Lambda), \quad \text{and } \Lambda = \exp[-E_g/(kT)].$$

Also, d_L in Eq. (16) in Ref. 7 has become $d_L = v_0^{1/3} \{r + f[(1 + 2\nu)/3]\}$ + $(a - v_0^{1/3})$ in this paper.

4. RESULTS AND DISCUSSION

4.1 General Summary Remarks

This paper summarizes theoretical results [4] calculated for the nematic (N), re-entrant N, smectic-A_d (SA_d), and smectic-A₁ (SA₁) LC phases and the I liquid phase. In the LC phases, the molecules have partial orientational order, with the long axes of the rigid rodlike cores tending to align parallel to a preferred axis (axis z) in the system.

The molecules in the SA₁ and SA_d phases have total and partial one-dimensional positional order, respectively, such that oriented molecules position into layers with the planes of these layers perpendicular to the z axis. [There is no positional order (regular spacing) along the x- and y axes in these SA phases.] The positional order of oriented molecules along the z axis in the SA₁ phase is such that the rigid cores pack with other rigid cores, and the semiflexible tail-chains pack with other tail-chains. In the SA_d phase, the cores and tails on oriented molecules each tend to pack with other like molecular parts. In the SA phases, L is the layer thickness, and d_L is the actual length of the molecule. In the SA₁ phase, $L = d_L$. The SA_d phase is a type of incommensurate phase since $L \neq d_L = 2L$. The flexibility of the tail-chains in smectic LC phases provides enough entropy (disorder) to keep the rigid cores from crystallizing totally, thus allowing the existence of partial positional order in smectic phases[4].

In the following theoretical results, the number of rigid segments (sites) r in the core of a molecule is 4. In each molecule, tail-chain 1 is $-(CH_2)_3-CH_3$ and tail-chain 2 is $-(CH_2)_y-CH_3$, with $y = f_2 - 1$.

In the particular calculations whose results are shown in the figures of this paper, these phase transitions were found to be second-order: SAD-N (except as noted), and SA1-SAD. In these calculations, these phase transitions were found to be weakly first-order: N-I, SAD-I, and SA1-I.

4.2 Hard Repulsions Generate I, N, Re-entrant N, SAD, and SA1 Phases

As seen in Table I, site-site hard [i.e., steric (infinitely large)] repulsions are sufficient [4] to generate N, low-T N (including re-entrant N), and multiple SA LC phases and the I liquid phase. (A re-entrant phase is a less-ordered phase that re-enters or re-appears at T below more-ordered phases.) Since there are no attractions, larger P and smaller T are needed for condensed-phase densities in Table I. (The transition between the high-T N phase and the SAD phase in column 1 of Table I is weakly first-order.)

Table I. Phases and transition T for $f_2 = 8$ and only hard repulsions

P =	149 atm	198 atm	149 atm	198 atm
$E_g/k =$	400 K	400 K	250 K	250 K
	I	I	I	I
	71.1 K	88.9 K	63.6 K	91.7 K
	N			
	70.1 K			
				SA1
				88.0 K
	SAD	SAD	SAD	SA1
	67.5 K	82.6 K	57.3 K	65.1 K
	N	N	N	N

In Table I, the general order of stable phases can be understood as follows. At higher T, the volume of the system is large enough that the molecules can pack randomly (thus forming the I phase). As T decreases, the volume of the system decreases, and the molecules are forced to order partially into N or SA LC phases, in order to pack the molecules into this decreasing volume. In the N phase, the molecules are forced to orient partially. In the SA phases, the molecules also have segregated (thus, more efficient) packing of oriented molecules, such that rigid cores pack with other cores and semiflexible tail-chains pack with other tail-chains, the tail-chains bend and twist well around each other, but do not pack as well with the oriented rigid cores. As T decreases even further, the tail-chains stiffen somewhat (become less flexible), thus decreasing the packing differences between cores and tails. The need for segregated packing of cores and tails decreases and is overcome by the entropy of unsegregated packing, thus giving a low-T N phase. (See Ref. 4 for actual density values in these phases and for more discussion.)

4.3 Effects of Pressure

As can be seen by comparing columns 1 and 2 and columns 3 and 4 in Table I, increasing P favors SA (first SAd, and then SAl) phases over N phases. As P increases, the volume decreases, thus leading to the segregated packing of the SA phases.

4.4 Effects of Tail-Chain Flexibility

As can be seen by comparing columns 1 and 3 and columns 2 and 4 in Table I, decreasing E_g/k (i.e., making the tail-chains more flexible) generally favors SA phases (especially SAl phases) over N phases. As the tails become more flexible in a relatively dense system, the molecules are forced into the segregated packing of the SA phases. (See Ref. 4 for more discussion.)

4.5 Effects of Attractions and Soft Repulsions in Lennard-Jones Potentials

The addition[4] of LJ (12,6) potentials to the system of Table I adds London dispersion attractions and soft (finite-sized) repulsions to the system. As seen in Table II and elsewhere in this section, attractive forces pull the molecules closer together, thus allowing the condensed phases I, N, SAd, and SAl to exist at larger T and smaller P than in Table I. (Specifically, $P = 1$ atm in Table II and elsewhere in this section.) In Table II and elsewhere in this section, the rigid core corresponds to $-\text{CH}_2-\phi-\phi-\text{CH}_2-$. From experimental data for atoms and small groups of atoms, the input variables (for definitions, see Ref. 7) were estimated (Ref. 4) after the manner of Ref. 7 to be $\epsilon_{cc}/k = 300$ K and $\epsilon_{tt}/k = 150$ K.

Table II. Transition T for an LJ system at $P = 1$ atm and $E_g/k = 250$ K

f_2	$T_{\text{SAl-SAd}}$ [K]	$T_{\text{SAd-N}}$ [K]	$T_{\text{N-I}}$ [K]
4	180.4	187.8	327.0
5	214.4	225.5	343.0
6	252.4	268.1	368.1
7	283.9	300.2	385.8
8	330.9	344.3	411.9
9	356.2	367.6	430.2

The effect of the soft repulsions (the net effect of the London dispersion attractions and the soft repulsions) in the LJ systems in Table II and elsewhere in this section is to push molecules further apart than in the system in Table I with only hard repulsions. This phenomenon allows a subtle competition between energy and entropy in determining the relative stabilities of the SA and N phases. In general, energy favors the SA phases, since the dispersion attractive energies are larger between two core sites (with their benzene rings) than between a core site and a tail site, thus favoring the segregated packing of the SA phases. Entropy favors the positional disorder of the N phase.

Increasing E_g/k from 250 K in Table II to 400 K leads [4] to the following phases and transition T (in K): For $f_2 = 8$: SAl 396.4 SAd 395.5 N 430.2 I

to conditions for a re-entrant $\underline{N}$ phase between $f_2 = 8$ (with a high- $\underline{T}$ $\underline{N}$ phase) and $f_2 = 9$ (with a low- $\underline{T}$ $\underline{N}$ phase). While non-integer values of f_2 are not available experimentally in pure (single-component) LC systems, effective non-integer f_2 values are easily achieved experimentally in a mixture of LC components with different integer values of f_2 .

In the steric system of Table I, increasing E_g/k decreases the density ρ . In contrast, in the LJ systems of this section, increasing E_g/k increases ρ slightly, thus leading to higher- $\underline{T}$ SA phases. As E_g/k increases in these LJ systems, the tail-chains get even stiffer at low $\underline{T}$, thus leading to low- $\underline{T}$ $\underline{N}$ (including re-entrant $\underline{N}$) phases. (See Ref. 4 for more discussion.)

4.6 Effects of Dipolar Forces

In this section, large dipolar forces (corresponding to those in a rigid core of $-O-\phi-\phi-C=N-$) have been added[4] to the system of Table II. The input variables for the calculations in this section are the same as in Table II, except for these additions (for definitions, see Ref. 7): $\mu_D = 5.2$ D, $\alpha'_C = 24 \times 10^{-24}$ cm³, and $\alpha'_T = 2 \times 10^{-24}$ cm³.

Adding dipolar forces in this section to the nondipolar LC system of Table II leads [4] to the following phases and transition $\underline{T}$ (in K): For $f_2 = 4$: $\underline{N}$ 115.2 SAd 115.7 SA1. For $f_2 = 5$: SA1 160.7 SAd 163.2 $\underline{N}$ 384.0 I. Thus, adding dipolar forces here leads to conditions for a re-entrant $\underline{N}$ phase between $f_2 = 4$ (with a low- $\underline{T}$ $\underline{N}$ phase) and $f_2 = 5$ (with a high- $\underline{T}$ $\underline{N}$ phase). Dipolar forces orient the cores more and pull the molecules closer to hard-repulsive separations, thus favoring SA and low- $\underline{T}$ $\underline{N}$ (including re-entrant $\underline{N}$) phases. (See Ref. 4 for more discussion.)

5. CONCLUDING REMARKS

In this paper, we have shown theoretically how the following competing interactions in the packing of the molecules are important in determining the relative stabilities of the $\underline{N}$, re-entrant $\underline{N}$, SAd (incommensurate), and SA1 LC phases and the I liquid phase: tail-chain flexibility as a function of $\underline{T}$, μ as a function of $\underline{T}$, hard repulsions, soft repulsions, London dispersion attractions, and dipolar forces. The theoretical results summarized in this paper have reasonable physical explanations and have also been found[4] to be in agreement with available experimental data. (See Ref. 4 for more discussion.)

6. ACKNOWLEDGMENT

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7. REFERENCES

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