(1940).

[6] D. Pines, Phys. Rev. 95, 1090 (1954).

[7] M. Shimizu, J. Phys. Soc. Japan 15, 2220 (1960); R. A. Ferrell, Phys. Rev. 107, 450 (1957).

[8] K. Brueckner and K. Sawada, Phys. Rev. 112, 328 (1958); S. D. Silverstein, *ibid.* 130, 1703 (1963).

[9] C. Herring, *Magnetism IV*, edited by G. Rado and H. Suhl (Academic, New York, 1966).

[10] N. H. March and B. Donovan, Proc. Phys. Soc. (London) A67, 464 (1954).

[11] H. Kanazawa and N. Matsudaira, Progr. Theoret. Phys. (Kyoto) 23, 426 (1960).

[12] A. H. Wilson, Proc. Cambridge Phil. Soc. 49, 292 (1953); *The Theory of Metals* (Cambridge U. P., New York, 1953).

[13] J. E. Hebborn, J. M. Luttinger, E. H. Sondheimer, and P. J. Stiles, J. Phys. Chem. Solids 25, 741 (1964).

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# Simple Molecular Model for the Smectic *A* Phase of Liquid Crystals

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The Maier–Saupe model of the nematic phase with an orientational order parameter is extended to the smectic *A* phase by introducing a new order parameter, the amplitude of a density wave in the direction of the nematic preferred axis. Self-consistent equations for the two order parameters are derived from an anisotropic model interaction and are solved numerically. We calculate the order parameters, the entropy, and the specific heat as a function of temperature for several values of dimensionless interaction strength $\alpha$ for the smectic *A* phase. The transition temperatures plotted versus $\alpha$ provide a theoretical phase diagram which resembles experimental plots of transition temperature versus alkyl chain length for homologous series of compounds. The model qualitatively reproduces chemical trends in transition entropies. Experiments are suggested to measure the order parameters in the smectic *A* phase.

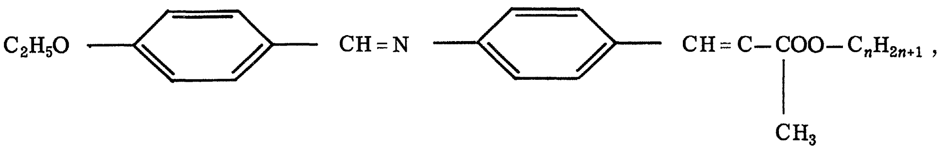
## I. INTRODUCTION

Maier and Saupe[1,2] have presented a molecular theory of the nematic phase in which the alignment of the molecules parallel to a preferred axis is described by an orientational order parameter. In this paper we extend the molecular model to the smectic *A* phase[3] by introducing another order parameter, the amplitude of a density wave in the direction of the preferred axis.

The textbook picture,[4,5] due to Friedel,[6] of the three phases of matter which we wish to discuss is shown in Fig. 1; the lines represent the long axis of the molecules. (i) At high temperature one has the isotropic liquid in which the positions of the centers of mass are random and the long axes point in random directions. The isotropic liquid is completely disordered, it is optically isotropic, and its x-ray diffraction pattern contains no sharp rings. (ii) At lower temperature some materials exhibit a nematic phase in which the centers of mass are still randomly placed but the long axes line up parallel to a preferred axis in space. The nematic phase is optically uniaxial but its x-ray pattern contains no sharp rings. The viscosity of this phase is low and it flows like a liquid. (iii) At still lower temperatures some materials exhibit the more highly ordered smectic *A* phase in which the long axes line up parallel to a preferred axis and the centers of mass sit on planes perpendicular to the preferred axis. The spacing between planes is approximately a molecular length and the centers of mass are presumed to move randomly in the planes. The smectic *A* phase is optically uniaxial and its x-ray pattern contains one sharp ring corresponding to the interplanar spacing ~ 20 Å.[7] The planes move freely over one another and the viscosity is low in the planar directions.

In these three phases the molecules are presumed to rotate freely about the long axis and to have no averaged dipole moment. There are occasionally other smectic phases at lower temperature and of course various crystalline phases.

As a concrete example consider the homologous series 4-ethoxybenzal-4-amino-*n*-alkyl-$\alpha$-methyl-cinnamate with the structure



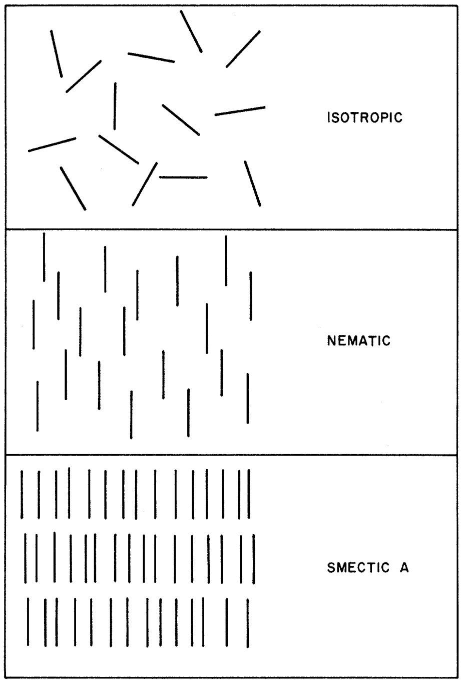


FIG. 1. Textbook picture of the isotropic liquid, the nematic, and the smectic *A* phases showing the orientational order in the nematic phase and planar structure of the smectic *A*.

which has been studied by Arnold.[8] Each member of this series exhibits the smectic *A*, nematic, and isotropic liquid phases in addition to the solid. The transition temperatures are shown in Fig. 7. The unsaturated central portion of this molecule is rigid and coplanar and defines a long axis; the alkyl end-chains are presumably flexible.

Maier and Saupe[1] introduced a molecular model for the interactions between anisotropic molecules and solved this model in the mean or self-consistent field approximation. The intermolecular potential, after averaging over the center-of-mass positions, is proportional to $-(\frac{3}{2}\cos^2\theta_{12}-\frac{1}{2})$, where $\theta_{12}$ is the angle between the directions of the long axes of the two molecules. The molecules prefer a parallel orientation of the long axes to minimize this anisotropic interaction. In the mean field approximation one introduces an orientational order parameter $\eta = \langle \frac{3}{2}\cos^2\theta_1 - \frac{1}{2}\rangle$, where $\theta_1$ is the angle between the long axis of one molecule and a preferred axis in space. One then finds a self-consistent equation for $\eta$ as a function of temperature. This model accounts qualitatively for a number of properties of the nematic phase which were inexplicable on the textbook picture; for example, the temperature dependence of the anisotropic dielectric constant and the dielectric relaxation.

In this paper we assume that the anisotropic interaction is short ranged and is proportional to $-\exp[-(r_{12}/r_0)^2](\frac{3}{2}\cos^2\theta_{12}-\frac{1}{2})$, where $r_{12}$ is the distance between centers of mass and $r_0$ is roughly a molecular length. With this potential and within the mean field approximation we show that it is energetically favorable for the oriented molecules to form a density wave which we assume to lie in the direction of the preferred axis. This density wave is described by the order parameter $\sigma = \langle\cos(\vec{r}\cdot\vec{q})(\frac{3}{2}\cos^2\theta-\frac{1}{2})\rangle$, where $\vec{q}$ lies in the direction of the preferred axis and is equal in magnitude to $2\pi$ divided by the interplanar distance. We find coupled self-consistent equations for the two order parameters $\sigma$ and $\eta$ as a function of temperatures. This model exhibits three phases: (i) the isotropic liquid with $\sigma = \eta = 0$; (ii) the nematic phase with $\sigma = 0$, $\eta \neq 0$; and (iii) the smectic *A* phase with $\sigma \neq 0$, $\eta \neq 0$. This model of the smectic *A* phase was also proposed very recently by Kobayashi.[9]

The purpose of the present paper is to present the model and to calculate its properties. It turns out that the model has one physical parameter $\alpha$ which acts as a dimensionless interaction strength for the smectic *A* phase. We will calculate the transition temperatures as a function of $\alpha$ and produce a generalized phase diagram for the isotropic-liquid–nematic–smectic-*A* system. We will also calculate the order parameters, the entropy, and the heat capacity as a function of temperature. We will compare the calculated transition entropies with experiment for several homologous series of compounds.

## II. THEORETICAL MODEL

In their work on the molecular model of the nematic phase Maier and Saupe considered the dispersion forces between anisotropic molecules and derived an anisotropic interaction between molecules averaged over a random distribution of their centers of mass

$$V_{12} = -(V_0/N)(\tfrac{3}{2}\cos^2\theta_{12}-\tfrac{1}{2}) , \qquad (1)$$

where $\theta_{12}$ is the angle between the directions of the long axis and $N$ is the density of molecules. Within the mean field approximation one assumes that each molecule feels an average potential of the form

$$V_1(\cos\theta) = -V_0(\tfrac{3}{2}\cos^2\theta_1-\tfrac{1}{2})\eta , \qquad (2)$$

where $\theta_1$ is the angle between the long axis of the molecule and the $z$ axis (the preferred axis). The molecular distribution function is then

$$f_1(\cos\theta) = \exp[(V_0\eta/kT)(\tfrac{3}{2}\cos^2\theta-\tfrac{1}{2})] . \qquad (3)$$

Using this distribution function and the two-body interaction (1) we recalculate the one-particle potential

$$V_1(\cos\theta_1) \equiv \frac{N\int d^3x_2\, d\Omega_2\, V_{12}(\cos\theta_{12}) f(\cos\theta_2)}{\int d^3x_2\, d\Omega_2\, f(\cos\theta_2)}$$

$$= - V_0(\tfrac{3}{2}\cos^2\theta_1 - \tfrac{1}{2})\langle(\tfrac{3}{2}\cos^2\theta_2 - \tfrac{1}{2})\rangle_f\,, \qquad (4)$$

where $x_2$ and $\Omega_2$ are the position and angular coordinates of molecule $z$, and the thermodynamic average is defined by

$$\langle A(\cos\theta)\rangle_f \equiv \frac{\int_0^1 d\cos\theta\, A(\cos\theta)\exp[(V_0\eta/kT)(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})]}{\int_0^1 d\cos\theta \exp[(V_0\eta/kT)(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})]}\,. \qquad (5)$$

The one-particle potential is self-consistent if the order parameter $\eta$ satisfies

$$\eta = \langle(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\rangle_f\,. \qquad (6)$$

This is the fundamental equation of the Maier-Saupe theory of the nematic phase which can be solved to find $\eta$ versus temperature.

In order to extend the Maier-Saupe model to the smectic $A$ phase, we assume a simple form for the anisotropic part of the interaction

$$V_{12}(r_{12}, \cos\theta_{12}) = -(V_0/Nr_0^3\pi^{3/2})e^{-(r_{12}/r_0)^2} \times(\tfrac{3}{2}\cos^2\theta_{12} - \tfrac{1}{2})\,, \qquad (7)$$

where $r_{12}$ is the distance between centers of mass and $r_0$ is of the order of the length of the rigid section of the molecule.

Now suppose that the molecules are preferentially oriented in the $z$ direction and that their centers of mass sit on planes parallel to the $x$-$y$ plane and intersecting the $z$-axis at 0, $\pm d$, $\pm 2d$, etc. The one-particle potential that a test molecule would feel is

$$V_1(z, \cos\theta) = - V_0\eta\,[1 + \alpha\cos(2\pi z/d)](\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\,, \qquad (8)$$

where

$$\alpha \equiv 2e^{-(\pi r_0/d)^2}\,, \qquad (9)$$

and we have neglected higher Fourier components of the potential.

The position of lowest potential energy of the test molecule is with the center of mass lying in one of the planes and with its long axis in the $z$ direction. Because of its thermal motion the long axis of the test molecule will rotate away from the $z$ axis and its center of mass will move out of the plane. It will still be preferentially oriented in the $z$ direction and it will prefer to sit near the planes; that is, there will be a density wave in the $z$ direction. The supposition that the other molecules sit on the planes is too simple and we must seek a self-consistent solution with a density wave in the $z$ direction. Motivated by the form of Eq. (8) we assume that the self-consistent one-particle potential is

$$V_1(z, \cos\theta) = - V_0[\eta + \sigma\alpha\cos(2\pi z/d)](\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\,, \qquad (10)$$

where $\eta$ and $\sigma$ are the order parameters. The one-particle distribution function is then

$$f_1(z, \cos\theta) = \exp[-V_1(z, \cos\theta)/kT]\,. \qquad (11)$$

Using this distribution function and the two-body interaction (7) we recalculate the one-body potential

$$\begin{aligned} V_1(z_1, \cos\theta_1) &\equiv \frac{N\int d^3x_2 d\Omega_2\, V_{12}(r_{12}, \cos\theta_{12})f(z_2, \cos\theta_2)}{\int d^3x_2 d\Omega_2 f(z_2, \cos\theta_2)} \\ &= - V_0[(\tfrac{3}{2}\cos^2\theta_1 - \tfrac{1}{2})\langle\tfrac{3}{2}\cos^2\theta_2 - \tfrac{1}{2}\rangle_f \\ &\quad + \alpha\cos(2\pi z_1/d)(\tfrac{3}{2}\cos^2\theta_1 - \tfrac{1}{2}) \\ &\quad \times\langle\cos(2\pi z_2/d)(\tfrac{3}{2}\cos^2\theta_2 - \tfrac{1}{2})\rangle_f]\,. \end{aligned} \qquad (12)$$

Self-consistency of (12) and (10) requires that

$$\eta = \langle(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\rangle_f\,, \qquad (13)$$

$$\sigma = \langle\cos(2\pi z/d)(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\rangle_f\,, \qquad (14)$$

where the average of a function of $z$ and $\cos\theta$ is defined by

$$\langle A(z, \cos\theta)\rangle_f \equiv \int_0^d dz \int_0^1 d\cos\theta\, A(z, \cos\theta)\frac{\exp\{(V_0/kT)[\eta + \sigma\alpha\cos(2\pi z/d)](\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\}}{\int_0^d dZ\int_0^1 d\cos\theta \exp\{(V_0/kT)[\eta + \sigma\alpha\cos(2\pi z/d)](\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})]\}}\,. \qquad (15)$$

Equations (13) and (14) must be solved self-consistently for the two order parameters $\eta$ and $\sigma$. The order parameter $\eta$ was introduced by Maier and Saupe and describes the orientational order; the order parameter $\sigma$ describes the amplitude of the density wave. Equations (13) and (14) exhibit three types of solutions: (i) $\eta = \sigma = 0$, no order characteristic of the isotropic liquid phase; (ii) $\sigma = 0$, $\eta \neq 0$, orientational order only, the theory reduces to the Maier-Saupe theory of the nematic phase; (iii) $\eta \neq 0$, $\sigma \neq 0$, orientational and translational order characteristic of the smectic $A$ phase.

In order to determine which of the three phases is stable at a given temperature we must calculate the free energy of the system. The entropy of $N$ molecules in the one-particle potential (10) is easily evaluated:

$$-TS = +NV_0(\eta^2 + \alpha\sigma^2) - NkT\ln\{d^{-1}\int_0^d dz\int_0^1 d\cos\theta \times\exp[(V_0/kT)(\eta + \alpha\sigma\cos(2\pi z/d))(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})]\}\,. \qquad (16)$$

The internal energy is just the thermodynamic average of the two-particle interaction

$$U = -\tfrac{1}{2} N V_0 \; (\eta^2 + \alpha\sigma^2) \,, \tag{17}$$

and the free energy is

$$F = U - TS \,. \tag{18}$$

Equations (13) and (14) for the order parameters can be found simply by minimizing the free energy with respect to the order parameters. Finally the specific heat at constant volume is given by

$$C_V = T \frac{\partial S}{\partial T} . \tag{19}$$

These are the equations which we need to calculate the physical properties of the model. In Sec. III we will solve these equations and calculate the transition temperatures and the order parameters, the entropy, and the specific heat as a function of temperature. Two physical parameters enter the theory: $V_0$ and $\alpha$. $V_0$ determines the nematic-isotropic transition temperature and fixes the temperature scale of the model. In what follows we will work with the reduced temperature $t = T/T_{\mathrm{NI}} = T/0.2202 V_0$. The one remaining parameter is $\alpha$ which is the dimensionless interaction strength for the smectic *A* phase. According to the model anisotropic interaction which we have used, we have

$$\alpha = 2 e^{-(\pi r_0/d)^2} ,$$

which can vary between 0 and 2. The interplanar distance is determined by the competition between the anisotropic forces which produce the smectic order and excluded volume effects. The smectic condensation energy is greater for larger values of $\alpha$, that is, for larger $d$. However, if one tries to make $d$ greater than the molecular length $l$ it is necessary to pack the molecules in the plane too closely together and this is energetically unfavorable. The most favorable situation is with $d$ of order $l$ as observed experimentally. Then the parameter $\alpha$ increases with increasing chain length of the alkyl tails. This is an important correlation which will be discussed in Sec. IV. The physical picture of the molecular interactions which leads one to this correlation is that the anisotropic interaction is due to the interaction of the rigid central section of the molecules and that the function of the flexible tail is merely to take up space and permit a larger interplanar spacing. The same function could be performed by an organic solvent and, according to this picture, one would expect $\alpha$ to increase with solvent fraction. One can, of course, choose not to believe this argument and regard the relationship between $\alpha$ and chain length, which is established in Sec. IV, as purely empirical.

We have assumed that the direction of the density wave $\vec{q}$ lies in the direction of the nematic preferred axis. Actually, with a separable model interaction of the form of (7) it is equally favorable energetically for the density wave to lie in any direction. This is a peculiarity of the model interaction and it is clear when one considers excluded volume effects that the density wave direction will coincide with the nematic preferred axis.

## III. NUMERICAL RESULTS

In this section we will solve the self-consistency equations (13) and (14) and calculate the order parameters, the entropy, and the specific heat as a function of temperature for several values of interaction strength $\alpha$.

In order to solve (13) and (14) we must be able to perform the integration over $z$ and $\cos\theta$. To do this we first expand $f(z, \cos\theta)$ as a power series in $\sigma$; for each term in the power series the $z$ integration is easy and we must evaluate integrals of the form

$$\int_0^1 (\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})^m \exp\!\left(-\frac{\eta}{t\,0.2202}(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\right) d\cos\theta$$

numerically. We keep as many terms in the power series (usually 10–20) as necessary to obtain the desired accuracy. In order to solve the self-consistency equations we choose a value for $\sigma/t$. We then choose a trial value of $\eta/t$ and use Eq. (14) to determine $t$. Equation (13) will not be satisfied and we must plot $\eta - \langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2} \rangle$ versus $\eta/t$ to find the value of $\eta/t$ for which $\eta = \langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2} \rangle$. We now have the values of the two order parameters $\eta$ and $\sigma$ at one temperature and can calculate the free energy and entropy. This calculation is performed as a function of temperature and we find $C_V$ from the entropy difference at two successive temperatures. When the phase transition is first order one must compare the free energies in the two phases at the same temperature to establish which phase is more stable.

The transition temperatures as a function of the parameter $\alpha$ are shown in the "phase diagram" Fig. 2. For $\alpha < 0.98$ the nematic-isotropic transition is $T_{\mathrm{NI}} = 1$ (in units of $0.2202 V_0$) and the entropy change at the transition is $\Delta S_{\mathrm{NI}} = 0.429 R_0$ [$R_0 = 1.986$ cal/(deg mole) = 8.31 J/(deg mole)]. These are just the values given by the Maier-Saupe theory since our theory reduces to the Maier-Saupe theory in the nematic phase. The smectic-*A*–nematic transition temperature is an increasing function of $\alpha$ and reaches $T_{\mathrm{NI}}$ at $\alpha = 0.98$. The smectic-*A*–nematic phase transition is second order for $\alpha < 0.70$ and is first order for $0.70 < \alpha < 0.98$. The entropy change at the smectic-*A*–nematic transition increases from 0 at $\alpha = 0.70$ to $1.18 R_0$ at $\alpha = 0.98$. For $\alpha > 0.98$ the smectic *A* phase melts directly into the isotropic phase and the entropy change is greater than $1.68 R_0$.

To illustrate the three types of behavior, we plot

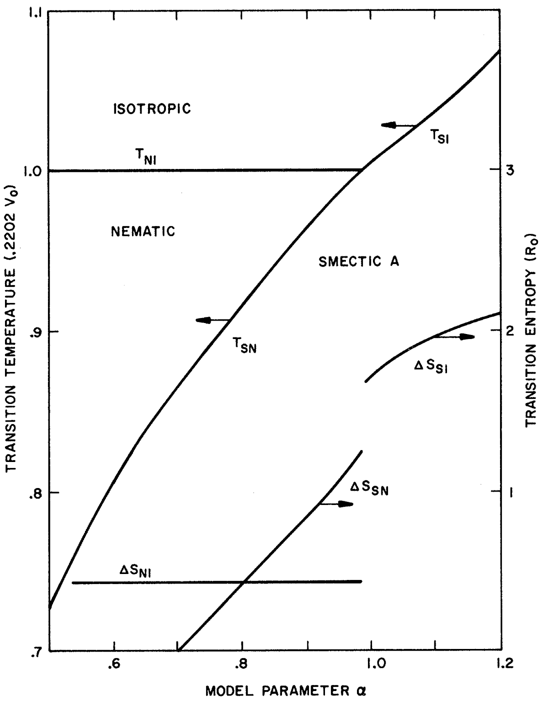


FIG. 2. Phase diagram for theoretical model parameter $\alpha$. Transition entropies are also shown.

the order parameters, the entropy, and the heat capacity versus temperature for three values of $\alpha$. For $\alpha = 0.6$ (Fig. 3) the smectic-$A$–nematic transition is second order ($T_{SN}/T_{NI} = 0.805$) and the smectic $A$ order parameter $\sigma$ falls continuously to 0. For $\alpha = 0.85$ (Fig. 4) the smectic-$A$–nematic transition is first order ($T_{SN}/T_{NI} = 0.940$) and the smectic $A$ order parameter $\sigma$ drops discontinuously to 0. Note that the smectic $A$ and nematic order parameters are coupled together and the nematic order parameter $\eta$ also drops discontinuously at $T_{SN}$. For $\alpha = 1.1$ (Fig. 5) the smectic $A$ phase melts directly into the isotropic phase ($T_{SI}/0.2202\,V_0 = 1.038$) and both order parameters drop discontinuously to 0. The transition temperatures and entropy changes for several values of $\alpha$ are listed in Table I.

## IV. COMPARISON WITH EXPERIMENT

### A. Phase Diagram

There have been extensive studies of the liquid-crystal transition temperatures in homologous series of compounds as a function of the number of carbon atoms in the alkyl endchains. According to Gray[4] the most common type of phase diagram that one finds is sketched in Fig. 6. For short chain lengths, one finds the sequence of phases: isotropic-liquid–nematic–smectic $A$ with decreasing temperature. With increasing chain length, the smectic-$A$–nematic transition temperature rises and meets the nematic-isotropic transition temperature. For large chain lengths one has only the smectic $A$ and isotropic phases. The other types of observed phase diagrams can be regarded as portions of this diagram. There are, of course, other smectic phases[3] which we omit from this discussion. From the thermodynamic point of view, the cholesteric phase is a slight modification of the nematic phase. The terms in the free energy which give rise to the cholesteric twist are very small and are unimportant for the thermodynamics. Thus we can compare the theoretical model with both nematic and cholesteric materials.

We have argued that the parameter $\alpha$ should increase with increasing chain length. Therefore the theoretical phase diagram (Fig. 2) of transition temperature versus $\alpha$ can be compared with the experimental phase diagram (Fig. 6). The similarity is obvious. Note that the variation of the parameter $V_0$ which determines $T_{NI}$ according to the Maier-Saupe theory is outside the scope of the model and we hold $V_0$ fixed. According to the theoretical model the $T_{SI}$ curve is very nearly a continuation of the $T_{SN}$ curve, whereas experimentally the $T_{SI}$ curve is a continuation of the $T_{NI}$ curve. We can claim,

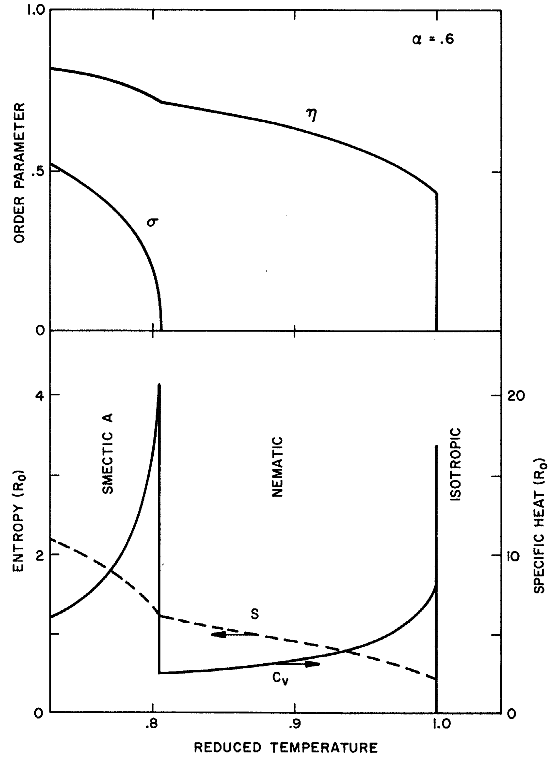


FIG. 3. Order parameters $\eta$ and $\sigma$, entropy $S$, and specific heat $C_v$ vs reduced temperature $kT/0.2202V_0$ for the theoretical model with $\alpha = 0.6$ showing the second-order smectic-$A$–nematic transition and the first-order nematic–isotropic-liquid transition.

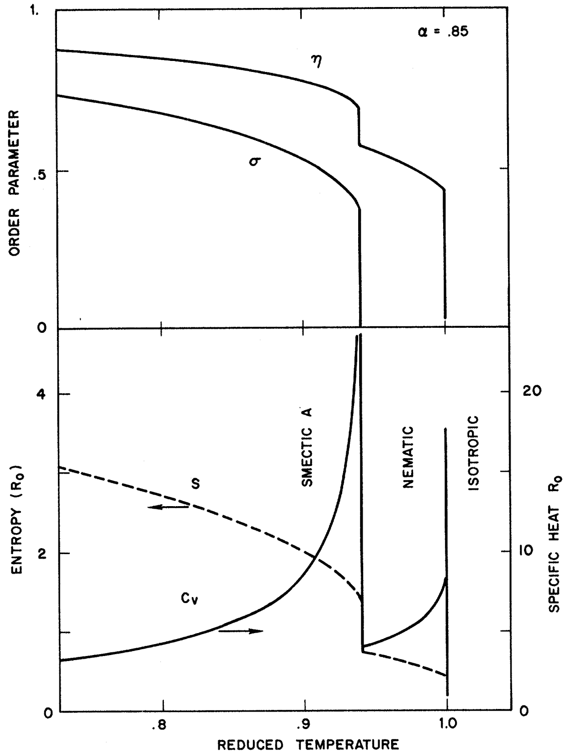


FIG. 4. Order parameters, entropy, and specific heat vs reduced temperature for $\alpha = 0.85$ showing the first-order smectic-$A$–nematic transition.

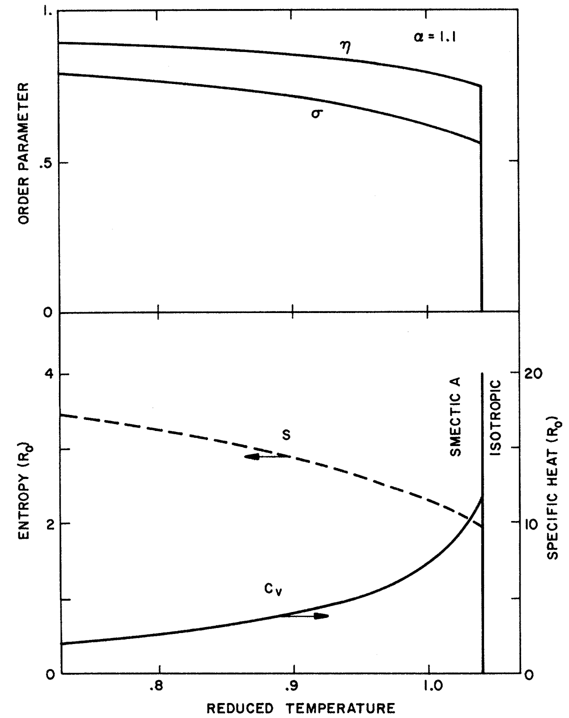


FIG. 5. Order parameters, entropy, and specific heat vs reduced temperature for $\alpha = 1.1$ showing the first-order smectic-$A$–isotropic-liquid transition.

however, to have a qualitative explanation of the experimental phase diagram.

### B. Transition Entropies

One striking feature of the theoretical model is that it predicts a second-order smectic-$A$–nematic phase transition for $T_{SN}/T_{NI} < 0.87$ and a first-order transition with increasing transition entropy for larger values of $T_{SN}/T_{NI}$ (see Fig. 2). In Figs. 7 and 8 we show experimental transition entropies for two homologous series—one nematic[8] and one cholesteric[10] material—exhibiting this trend of increasing $\Delta S_{SN}$ with increasing $T_{SN}/T_{NI}$. We can get a parameter-free comparison of theory with experiment by plotting $\Delta S_{SN}$ versus $T_{SN}/T_{NI}$ as in Fig. 9. The solid line is the theoretical curve and the circles and triangles are the experimental entropy changes from Figs. 7 and 8. While the experimental trends are correctly predicted the experimental magnitudes of the transition entropies are a factor of two to three less than that theory predicts. There are probably two reasons for this magnitude discrepancy. The mean field approximation overestimates transition entropies by lumping together pretransition, transition, and post-transition entropies. Secondly, the first-order character of this transition arises from the coupling of the density wave to the orientational order. The theoretical model assumes that only anisotropic forces contribute to the stability of the smectic $A$ phase and thus overestimates this coupling and overestimates the first-order nature of the transition. The second-order region of the phase diagram has not been identified experi-

TABLE I. Reduced transition temperatures and transition entropies (in units of $R_0$) as a function of model parameter $\alpha$. For $\alpha < 0.098$, $T_{NI}/0.2202V_0 = 1$ and $\Delta S_{NI} = 0.429$.

| $\alpha$ | $T_{SI}/0.2202V_0$ | $\Delta S_{SI}$ |
|---|---|---|
| 2.0 | 1.398 | 2.52 |
| 1.5 | 1.192 | 2.35 |
| 1.2 | 1.074 | 2.11 |
| 1.1 | 1.038 | 1.96 |
| 1.05 | 1.021 | 1.86 |
| 1.0 | 1.005 | 1.72 |
| $\alpha$ | $T_{SN}/0.2202V_0$ | $\Delta S_{SN}$ |
| 0.98 | 0.998 | 1.224 |
| 0.95 | 0.985 | 1.066 |
| 0.90 | 0.964 | 0.845 |
| 0.85 | 0.940 | 0.633 |
| 0.80 | 0.916 | 0.431 |
| 0.75 | 0.892 | 0.216 |
| 0.70 | 0.866 | 0 |
| 0.65 | 0.837 | 0 |
| 0.60 | 0.805 | 0 |
| 0.55 | 0.769 | 0 |
| 0.50 | 0.728 | 0 |

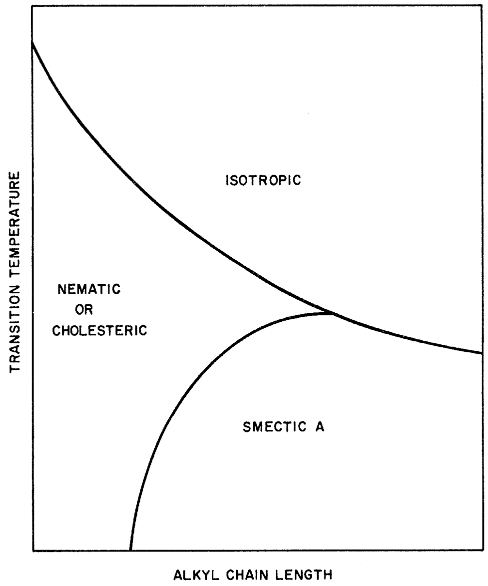


FIG. 6. Typical phase diagram for homologous series of compounds showing transition temperatures vs length of the alkyl endchains.

mentally but it would require very careful specific heat measurements to do so. The model predicts a constant transition entropy $= 0.429 R_0$ at the nematic–isotropic-liquid transition, whereas experimentally[8] this transition entropy is observed to increase with increasing chain length from $0.06 R_0$ to $0.35 R_0$ for the nematic material of Fig. 7. The smectic-$A$–isotropic transition entropy $\Delta S_{SI}$ increases from $1.68 R_0$ at $\alpha = 0.98$ to $2.52 R_0$ at $\alpha = 2$ according to the model. In the homologous series 4-4′ azoxy-di($n$-alkyl-$\alpha$-methyl cinnamate) Arnold[8] finds that $\Delta S_{SI}$ increases from $1.0 R_0$ at $n = 4$ to $3.0 R_0$ at $n = 12$. The first two members of this series $n = 2, 3$ exhibit a nematic phase so that $n = 4$ should correspond to $\alpha \approx 1$. The qualitative trend and the order of magnitude of $\Delta S_{SI}$ are correctly predicted.

### C. Specific Heat

Transition entropies have been published for several homologous series of compounds; however, only in a few cases have the full specific heat curves been published. Here we compare the calculated specific heat with Arnold's[8] data for cholesteryl myristate. The specific heat changes due to the phase transitions sit on top of a large background specific heat due to the internal motion of the molecules. We estimate this background by fitting the specific heat in the isotropic liquid with a straight line and extrapolating into the liquid crystal phases. This procedure is probably safe in cholesteryl myristate since the isotropic liquid specific heat is observed to be linear over a large temperature region. The experimental specific heat, with the background subtracted, is shown in Fig. 10 versus reduced temperature $T/T_{CI}$. The entropy is obtained by integrating the specific heat curve. In order to compare the model with experiment we choose $\alpha = 0.95$ so that the ratio of transition temperatures $T_{SC}/T_{CI}$ is equal to the experimental ratio 0.986. The theoretical specific heat and entropy are plotted as solid lines in Fig. 10. The specific heat and entropy in the smectic $A$ phase are in rather good agreement with the experiment. However, the details of the transition region are not well described by the theory. The theoretical specific heat in the cholesteric phase is far too small and the transition entropy at the smectic-$A$–cholesteric transition is too large. The transition entropies and the entropy at $T/T_{CI} = 0.95$ are compared in Table II. One expects deviations of this sort when one uses the mean field approximation. In the mean field approximation, pretransition and post-transition effects are not treated properly and these entropy contributions are lumped into the transition entropy.

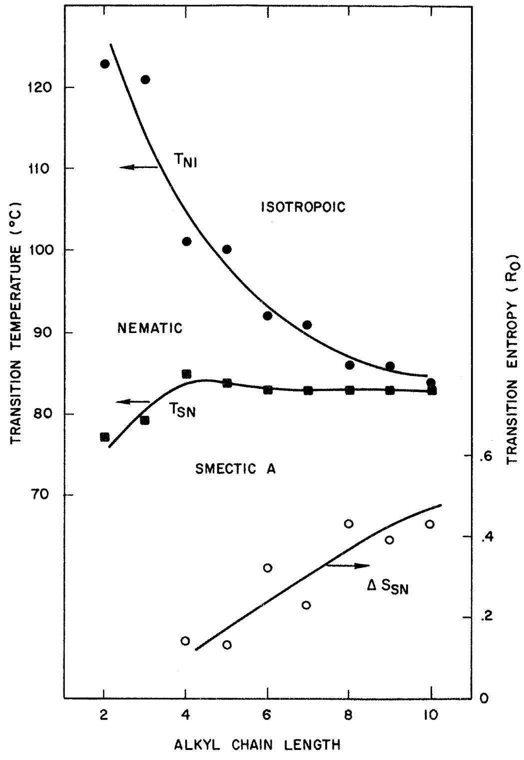


FIG. 7. Transition temperatures and transition entropy of 4-ethoxybenzal-4-amino-$n$-alkyl-$\alpha$-methyl cinnamate vs alkyl chain length from Ref. 8. Filled circles denote nematic-isotropic transition temperature; squares denote smectic-$A$–nematic transition temperature; and open circles denote smectic-$A$–nematic transition entropies. The lines are drawn as a guide to the eye.

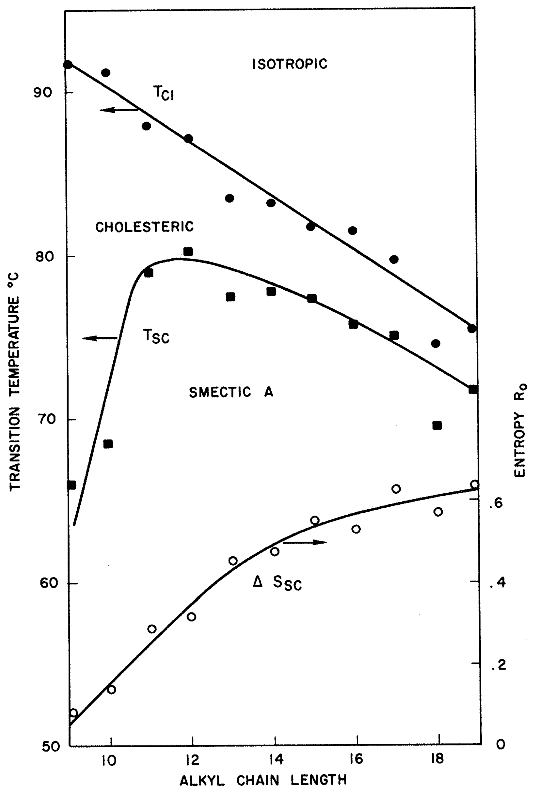


FIG. 8. Transition temperatures and transition entropy of cholesteryl esters of saturated aliphatic acids vs alkyl chain length from Ref. 10. Filled circles denote the cholesteric–isotropic-liquid transition temperature; squares denote the smectic-*A*–cholesteric transition temperature; and open circles denote the smectic-*A*–cholesteric transition entropies.

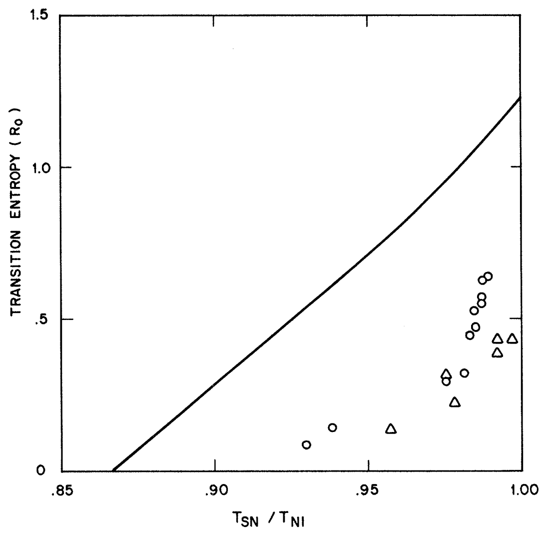


FIG. 9. Smectic-*A*–nematic (or cholesteric) transition entropy versus ratio of transition temperatures $T_{SN}/T_{NI}$. Solid line is the theoretical curve taken from Fig. 2; open circles are the experimental data from Fig. 8; and open triangles are from Fig. 7.

## V. CONCLUSIONS

We have presented a simple molecular model with anisotropic forces and shown that, within the mean field approximation, the model exhibits three phases: an isotropic liquid, a nematic, and smectic *A* phase. The nematic phase is described by an orientational order parameter $\eta = \langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \rangle$ and in the smectic *A* phase one has in addition a density-wave order parameter $\sigma = \langle \cos(2\pi z/d)(\frac{3}{2}\cos^2\theta - \frac{1}{2}) \rangle$. The self-consistency equations for these order parameters were set up and solved to find the temperature dependence of the order parameters, the entropy, and the specific heat. By plotting the transition temperatures versus the interaction strength $\alpha$ we found a phase diagram similar to that for a homologous series of compounds. The trends and order of magnitudes of transition entropies were found to be correctly predicted by the model. The experimental evidence that we have examined indicates that the theoretical model is a satisfactory qualitative model for the smectic *A* phase.

The assumed molecular order in the various phases is as follows (assuming rigid molecules): (i) In the isotropic liquid there is free rotation of the long axis of the molecules, free rotation about the long axis, and random motion of the centers of mass in three dimensions. (ii) In the nematic phase the long axes line up preferentially parallel to a direction in space and there is free rotation about the long axis, and random motion of the centers of mass in three dimensions. (iii) In the smectic *A* phase the long axes line up preferentially parallel to a direction in space, there is free rotation about the long axis, the centers of mass sit preferentially near planes normal to the preferred axis with an interplanar spacing of the order of the molecular length (the one-dimensional density wave), and the centers of mass move randomly in the planes. In all these phases if the molecules are asymmetric and have a dipole moment it is assumed that the dipole moments are not aligned.

It is worthwhile to list some of the assumptions and approximations which we have made. (i) We began with a grossly oversimplified intermolecular potential (7). The connection between this model

TABLE II. Transition entropies and entropy at $T/T_{CI} = 0.95$ for the theoretical model ($\alpha = 0.95$) and for cholesteryl myristate.

| | Theory | Experiment |
|---|---|---|
| $\Delta S_{CI}$ | 0.43 | 0.51 |
| $\Delta S_{SC}$ | 1.07 | 0.61 |
| $S$, $T/T_{CI} = 0.95$ | −2.04 | −2.4 |

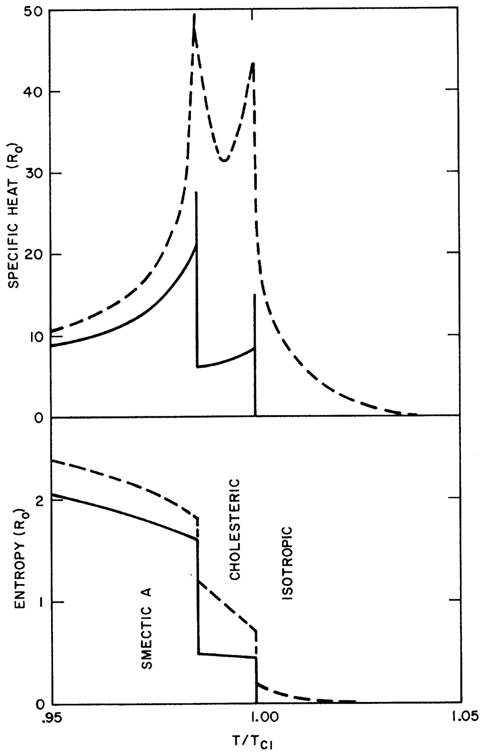


FIG. 10. Comparison of theoretical specific heat and entropy with experiment. Solid lines are from the theoretical model with $\alpha = 0.95$ and the dashed lines are from Arnold's data on cholesteryl myristate (Ref. 8).

potential and the structure of the molecule has not been elucidated although we have suggested that increasing the endchain length does not affect the model interaction but rather permits a larger interplanar spacing and a larger value for the parameter $\alpha$. (ii) We have worked within the mean field approximation which neglects short-ranged order and the effects of the fluctuations of the order parameters. (iii) We have assumed a model of rigid molecules which means, in effect, that we have assumed that the internal motions of the molecules are not affected by the phase transitions.

A number of experiments are suggested by the present work. One can measure the smectic *A* order parameter $\sigma$ directly by measuring the integrated intensity of the smectic x-ray ring versus temperature. This intensity, which should be approximately proportional to $\sigma^2$, can probably be normalized to an equivalent ring in the powder pattern for the solid. One could measure the nematic order parameter $\eta$ in the smectic *A* phase by any of the methods used in the nematic phase, for example, from the anisotropy of the index of refraction. The values for $\alpha$ which we find by fitting the transition temperature ratio are a decidedly nonlinear function of chain length, whereas one would expect a linear variation. It would be interesting to measure the interplanar spacing *d* for a homologous series for which thermodynamic data are available, since the model provides a direct relationship between $\alpha$ and *d*. It would be most useful in assessing the quantitative validity of the model to have a broader comparison with accurate specific heat data. It would be interesting to know whether the smectic-*A*–nematic transition actually becomes second-order for small $T_{SN}/T_{NI}$. Smectic-nematic transitions with small $T_{SN}/T_{NI}$ have been observed by Arora *et al.*[11] and are good candidates for this second-order transition.

On the theoretical side it should be possible to extend the model to the more highly ordered smectic phases. It would be interesting to study the effects of fluctuations of the smectic *A* order parameter on various properties of the nematic and cholesteric phases. One expects these fluctuations to affect the smectic-*A*–nematic transition temperature and even the nematic-isotropic transition temperature near the triple point. The connection between the model parameters and the molecular structure deserves some attention.

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[1] W. Maier and A. Saupe, Z. Naturforsch. 13A, 564 (1958); 14A, 882 (1959); 15A, 287 (1960).

[2] G. Meier and A. Saupe, in *Liquid Crystals*, edited by Glen H. Brown, G. J. Dienes, and M. M. Labes (Gordon and Breach, London, 1966), p. 195.

[3] H. Sackmann and D. Demus, in Ref. 2, p. 341.

[4] G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals* (Academic, New York, 1962).

[5] I. G. Chistyakov, Usp. Fiz. Nauk 89, 563 (1966) [Sov. Phys. Usp. 9, 551 (1967)].

[6] G. Friedel, Ann. Phys. (Paris) 19, 273 (1922).

[7] Hermann, Z. Krist. A92, 49 (1935).

[8] H. Arnold, Z. Physik Chem. (Leipzig) 239, 283 (1968); 240, 185 (1969).

[9] K. K. Kobayashi, Phys. Letters 31A, 125 (1970); J. Phys. Soc. Japan 29, 101 (1970).

[10] G. J. Davis and R. S. Porter, Mol. Cryst. Liquid Cryst. 10, 1 (1970).

[11] S. A. Arora, J. L. Fergason, and A. Saupe, Mol. Cryst. Liquid Cryst. 10, 243 (1970).