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Richard Alben [a]

[a] Yale University, Department of Engineering and Applied Science, New Haven, Connecticut, 06520

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Pretransition Effects in Nematic Liquid Crystals: Model Calculations†

RICHARD ALBEN

Yale University
Department of Engineering and Applied Science
New Haven, Connecticut 06520

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Abstract—Calculations of the properties of some lattice models and continuum models of a hard rod liquid with and without attractive energies are presented. The theory is of the " molecular field " variety in that short-range-order is neglected. Both the long-range-order parameter and the density are varied to obtain the state of minimum Gibbs free energy at given pressures and temperatures. Among the properties reported are expansivity, compressibility and specific heat. Each of these displays pretransition effects qualitatively similar to those seen on the low temperature side of nematic liquid crystal–isotropic liquid phase transitions. There are important quantitative discrepancies however. It appears that the discrepancies are due more to the approximate nature of solutions than to the idealizations of the models. The " near critical " nature of liquid crystal phase transitions cannot be well described in terms of long-range-order alone.

One gross error of the hard-rod models can, however, be remedied. The coexistence curves for real materials are far from being isochores; hard rod packing effects, although apparently important, do not explain the transition. Thus an order dependent energy is introduced. Results for some optimally fitted models are compared with experiment.

1. Introduction

One of the striking features of the nematic liquid crystal to isotropic liquid phase transition is the presence near the transition of precursor effects in both ordered(1–6) and disordered phases.(7–9) Another striking feature is the relatively large sensitivity of the transition temperature to changes in pressure.(10,11) Both of these features bear on the as yet unsettled problem of the underlying interactions which cause the rod-like molecules of nematogenic substances to become aligned in the nematic state.

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Calculations relating to two distinct types of mechanisms have appeared. Ordering due to orientation-dependent attractive energies between molecules has been treated by Weber,$^{(12)}$ Maier and Saupe,$^{(4)}$ and others.$^{(13-15)}$ Order due to the repulsive interactions of impenetrable but otherwise non-interacting rods has been treated by Onsager,$^{(16)}$ Flory$^{(17)}$ and others.$^{(18-23)}$ Previous model calculations,$^{(17-21)}$ however, do not contain results for which both density and order parameter are allowed to seek their equilibrium values at given temperature and pressure. Thus no broad-based comparison between theory and experiments relating to liquid crystals was possible.

In this paper calculations for model systems of hard rods with orientational phase transitions are reported. The theory is of the " molecular field " type in that short range order is neglected. As far as possible within the limitations of our approximations, we exhibit the structure of packing-effect-induced phase transitions in idealized systems and then elucidate the roles of various interaction mechanisms in determining experimentally accessible quantities. The properties computed are Gibbs free energy, volume, entropy, order parameter, isobaric expansivity (α), isothermal compressibility (β), and specific heat at constant pressure (C), all as functions of temperature and pressure. Only pretransition effects in the ordered phase, as opposed to post-transition, effects in the disordered phase, are discussed as the latter do not appear in the theory. Nor do we treat dynamical effects.

Frankly, it is difficult to extract conclusions which are truly relevant to measurable effects from our approximate model calculations. Indeed, in the strict sense it has not been proved that hard rods form a long-range-ordered state at all! Still, we venture the following conclusions:

(a) There are pretransition effects for systems which order because of the repulsive " packing " effects alone; and, a long-range-order theory can describe them partially. However, the theory succeeds less well than, for example, molecular field theories of magnetism. It may be surmised from this, and from experimental facts,$^{(7,13,24)}$ that short-range-order is relatively more important here. The short-range-order cluster parameter, introduced by Maier and Saupe$^{(4)}$ to rectify disagreements in the transition volume discontinuity, does not suffice for pretransition effects in the " thermodynamic compliances ", α, β and C. Some extrapolations made by previous authors$^{(13,20)}$ using long-range-order-only theories are shown to have been unwarranted.

(b) The coexistence curves of real materials in the P–T plane cannot be explained by packing effects of hard rods alone. An order dependent energy, a temperature dependent geometry, or a combination of energetic and geometrical effects is required. Without specific knowledge regarding the temperature and volume dependence of all interactions, it is not possible to tell what fraction of relevant interactions are of geometrical origin. It can be said, however, that the V^{-2} dependent energy of order, proposed by Maier and Saupe and verified (but only weakly) by some experiments,$^{(25,26)}$ is sharply inconsistent with observed coexistence curves.

(c) The most important hoped-for result of this work is to display the basic limitations of the long-range order approach as applied to liquid crystal models. The limitations are in some respects severe. The disagreements between theory and experiment are probably due to the long-range-order approximation and not to idealizations of the models. Thus the treatment of short-range-order, rather than more realistic models, appears to be the fruitful path for future research.

This paper contains five sections and an appendix. Section 2 is a discussion of the conceptual basis of long-range-order model theories. In Sec. 3 we present a solution for a lattice model in which the order is associated entirely with the packing mechanism. We discuss the mathematical structure of the solutions using the concepts of packing and mixing entropies, and elastic energy of transition. Changes in the balance between these competing effects are directly related to the onset of the orientational phase transition. In Sec. 4 we consider a continuum model where the packing mechanism is treated in analogy to the lattice case. In order to show its influence on the coexistence curve, the energy mechanism is introduced phenomenologically. Some results regarding the mathematical structure of this transition are presented and compared with those for the lattice model. Also, calculated pretransition effects and other properties are used to elucidate the relative roles of the energy and the packing mechanisms. In Sec. 5 we briefly review our conclusions from the model calculation, relate them to previously published results on long-range-order theories, and discuss their possible experimental significance in view of the approximations used. Finally, in the Appendix we describe our numerical methods for dealing with constant pressure processes.

2. Long-Range-Order Model Theories

In the model theories of the next two sections we compute bulk thermodynamic properties through the use of an approximation which allows the delicate problem of calculating the orientation and position-dependent correlation function for anisotropic particles to be circumvented.. The approximation is that there are no positional fluctuations in the density of particles or in the distribution of their axes of orientation. That is, " short-range-order " is neglected. We describe below in general terms the nature of the long-range-order-only theory and indicate how the inclusion of short-range-order would modify its results.

We always will treat attractive energies in a mean field approximation which need not be discussed here (see Sec. 4). The subtle point is the configurational entropy of packing. By this we mean the number of ways of placing rods in a given volume with a given distribution of axes of orientation but with no restriction on their position save that implied by mutual impenetrability. To compute the configurational entropy we must find the number of ways of placing a rod in a given orientation when a number of rods with a certain distribution of orientations have already been placed.

The number of ways of placing a given rod is found by multiplying: (i) the number of empty locations for a single point on the rod, by (ii) the probability that no rod already present will interfere as the rod is built up from a point to full size. The probability of non-interference is determined by the average volume which the presence of the added rod excludes to the other rods already present. Clearly the larger the excluded volume, the less the chance of successfully building up the rod. Since the volume a given rod excludes to a rod perpendicular to it is of order: length × length × diameter, while the volume excluded to parallel rods is only: length × diameter × diameter, long rods will have the largest entropy of packing if they are parallel. The rods will not be perfectly parallel because of the effect of mixing entropy (see Sec. 3), but the packing entropy can cause the rods to become very highly ordered.

The trouble with the above procedure is the neglect of fluctuations (short-range-order). The probability of success in placing a rod is more properly an averaged function of the local order rather than a function of the average order. The reader may readily convince himself (by considering the building up of very long rods in stages) that regions where order is locally favorable to a given direction contribute very strongly to the probability that a rod along that direction can successfully be added. Thus a fluctuation which did not change the average order would increase the probability of success since the added contribution from the favorable region would outweigh the diminution from the corresponding unfavorable region. The neglect of short-range-order thus leads to an underestimate of the entropy, especially for long rods and especially for states of low long-range-order. Because of this, we can encounter a case for the lattice model (Sec. 3) where the configurational entropy becomes negative while there is still room for all the rods. More importantly, our formulas for the variation of packing entropy with order are inaccurate.

In the succeeding treatment we make many approximations which expedite our computation of " background properties " and bear little on the orientational phase transition itself. The most important source of error regarding the transition is inexorably tied to the use of a long-range-order theory.

3. Lattice Model

Lattice models have long been used to study the configurations of flexible polymers in solution.(17,18,19) Their application to liquid crystals was implicit in the work of Flory(17) (1956) on rigid rods with an orientational phase transition. Flory's treatment, which formally at least is applicable to all densities and so to pure liquid crystals, will form the basis of our discussion. We reexamine the simplest version of the lattice model in some detail in order to clarify the mathematical structure of the phase transition as it appears in our variation of Flory's approximation. We present pretransition effects for an " athermal " case and also for a Van der Waals fluid.(27)

It is of considerable interest for future work on short-range-order that the simple lattice model, which is intrinsically the most tractible representation of a fluid-orientational phase transition yet devised, contains all of the essential features displayed by more complex cases.[A]

In our model, space is represented by a simple cubic array of cells. A rod (of length X) is a series of X full[B] cells running along one of the three cubic directions. We let there be M cells and N rods. The fraction of rods which point in the ith direction is given by α_i. The interaction between rods is contained entirely in the " hard core " requirement that no two rod segments may occupy the same site. The problem is to find the direction distribution $\{\alpha\}$ and the density N/M corresponding to the state of maximum Gibbs free energy for all values of the normalized pressure P/T in the usual thermodynamic limit that N and M are very large.

Because there is no interaction between sites, the Gibbs free energy may be found in terms of the configurational entropy, which we now discuss.

The possible configurations available to a lattice model are denumerable, a considerable simplification over real bodies occupying continuous space. Even so, except in special cases,[C] it is not possible to compute the configurational entropy exactly. An approximate procedure may be described in terms of a two-step process. The N rods are first segregated according to the directions in which they will point. Boltzmann's constant, k, times the number of ways of doing this, will be referred to as the entropy of mixing, S^{mix}. From a different point of view this represents the entropy increase when rods pointing in different directions are mixed.

$$S^{\mathrm{mix}} = k \log [N!/\Pi_i(\alpha_i N)!] \approx Nk\left(-\sum_i \alpha_i \log \alpha_i\right), \tag{1}$$

where we assume for the moment that the rods are distinguishable. S^{mix} is an entropy of disorder in the usual sense: it is largest for equal α's and smallest for the most ordered states (e.g., $\alpha_3 = 1$, $\alpha_1 = \alpha_2 = 0$) and it scales with N at constant $\{\alpha\}$.

In step 2 the rods are inserted successively into the lattice. Say the $(n+1)$st rod is to point in the direction i. The number of ways to place the first segment is just the number of empty sites, $M - nX$. The probability g_2^i that a neighbor (colinear along i) of the first empty site is itself empty (and thus ready to receive the next rod segment) is the ratio of empty sites to the sum of: (1) empty sites, (2) sites with $j \neq i$-directed rods and (3) sites with beginnings[D] of i-directed rods. That is:

$$g_2^i = \frac{M - nX}{M - n(X-1)\alpha_i'}, \tag{2}$$

where α_i' is the proportion of i-directed rods among rods already present. We next assume that the probability that each and every site up to the Xth site along i is empty, given that previous ones are, is:

$$(g_2^i)^{X-1}. \tag{3}$$

Thus the number of ways of placing the $(n+1)$st rod in the direction i is:

$$\frac{(M - nX)^X}{(M - n(X-1)\alpha_i')^{X-1}}. \tag{4}$$

The total number of ways of packing does not depend on the order in which rods are placed, a property preserved by Flory's approximation. We choose for convenience an order which keeps the distribution at each stage, $\{\alpha'\}$, constant and equal to the final distribution, $\{\alpha\}$, throughout the placement process. Then the properly weighted geometric mean number of ways of placing the $n+1$th rod is:

$$\frac{(M - nX)^X}{\Pi_i (M - (X-1)\alpha_i n)^{\alpha_i (X-1)}}. \tag{5}$$

With the help of the relation:

$$\prod_{n=1}^{N} (M - na)^a \approx M!/(M - Na)! \tag{6}$$

it is seen that the entropy of packing all N rods is:

$$\begin{aligned} S^{\text{pack}} &= k \log \frac{M!}{(M - XN)!} \Pi_i \frac{(M - (X-1)N\alpha_i)!}{M!} \frac{1}{N!} \\ &\approx Nk \frac{X}{f} \left[\sum_i \left(1 - \left(1 - \frac{1}{X}\right) f\alpha_i\right) \log \left(1 - \left(1 - \frac{1}{X} f\alpha_i\right)\right.\right. \\ &\qquad \left. - (1 - f) \log (1 - f) - \frac{f}{X} \log \frac{f}{X}\right] \end{aligned} \tag{7}$$

where f is a dimensionless density, $f = XN/M$, which gives the fraction of lattice sites which are full. (This is equivalent to DiMarzio's result.(19)) We have divided by $N!$ to account for the fact that the rods are indistinguishable. In contrast to S^{mix}, S^{pack} is greatest for orientationally ordered states. There is no paradox in this since, loosely speaking, S^{pack} measures positional disorder. Because colinear rods interfere less, positional disorder is favored by orientational order.

From (7) it is seen that the extent to which S^{pack} is affected by ordering is always a monotonic increasing function of f. The total configurational entropy is the sum of S^{mix} and S^{pack}, where S^{mix} is independent of f. Thus the distribution which maximizes the total entropy is isotropic or anisotropic in varying degree depending on the value of the density with highly ordered states favored by high density.

It will be recalled that our goal is to find the state, that is the density and distribution $\{\alpha\}$, which minimizes the Gibbs free energy G at a set pressure and temperature. As described in the Appendix, this may be accomplished by examining the distributions and pressures associated with minima in the Helmholtz free energy F at set densities and temperature. For this problem $F(f, T)$ is just $(-T)$ times the configurational entropy. The minimum condition, found by differentiating the sum of (1) and (7) with respect to $\{\alpha\}$ subject to the requirement that $\sum_i \alpha_i = 1$, yields an equation for each α_i which has the form:[E]

$$\alpha_i\left[\frac{1}{(1-(1/X))f}-\alpha_i\right]^{c_1}=c_2, \tag{8}$$

where c_1 and c_2 are constants. Equation (8) has at most two distinct solutions for $0 < \alpha_i < 1$ and so the minimum distribution has at least two of the α_i's equal. Without loss of generality therefore, we may take α_3 as the special α and define a parameter:

$$\eta = \tfrac{3}{2}(\alpha_3 - \tfrac{1}{3}), \tag{9}$$

which measures the extent to which rod orientations favor or disfavor the 3 axis. The solution to (8) displays a first order phase transition in which η plays the role of the order parameter. Depending on the values of f and X (density and length) a solution to (8) may correspond to $\eta = 0$ (isotropic phase) and one may correspond to $\eta > 0$ (anisotropic phase).[F] (For sufficiently long rods) we find that at high density there is only an anisotropic phase. For a range of lower densities both phases are local minima in F with the true equilibrium given by the phase of lowest G. Finally at sufficiently low densities the anisotropic phase minimum becomes an inflection point and disappears leaving only the isotropic phase. The conditions for which this happens will be denoted " critical " as they correspond to a local instability and are associated with divergences in compliance coefficients for the anisotropic phase. This use of " critical " does not imply a true equilibrium critical point. Indeed, the transition conditions, for which the equilibrium shifts from anisotropic to isotropic phase, always occur before the " critical " point can be reached from equilibrium anisotropic states.

The molar Gibbs free energy and the pressure are given by:

$$\frac{G}{RT} = \sum_i \alpha_i \log \alpha_i + \sum_i (X-1)\,\alpha_i \log\left(1-\left(1-\frac{1}{X}\right)f\alpha_i\right) - X\log(1-f) + \log\frac{f}{X} \tag{10}$$

$$\frac{PV_0}{RT} = \left\{\sum_i \log\left[1-\left(1-\frac{1}{X}\right)f\alpha_i\right] - \log(1-f)\right\}X \tag{11}$$

where V_0 is the molar volume at unit density and R is the gas constant. As described in the Appendix, the solution for all physically relevant properties is completed by numerically inverting (11) to obtain f and hence G as a function of P and T. Note that because there is no configuration dependent internal energy, the density and hence G/RT depend on P and T only through their ratio.

In Fig. 1 we display the value of η at the transition and critical points as a function of rod length(20)—including the formally allowable solutions for non-integral X. The general behavior is interesting but, as we now argue, not directly related to an exact solution. First let us introduce the concept of " elastic energy of transition ". By this we refer to the difference between ΔF and ΔG where ΔF is the change in Helmholtz free energy upon disordering at constant volume and ΔG is the change in Gibbs free energy upon disordering at constant pressure. The latter quantity governs the transition, the former is mathematically more accessible, and the elastic energy provides a link between them. The transition is taken as two steps: (1) disordering at constant V and (2) expansion to relieve the excess pressure P^{ex} which appears after step 1. (P^{ex} is associated with the

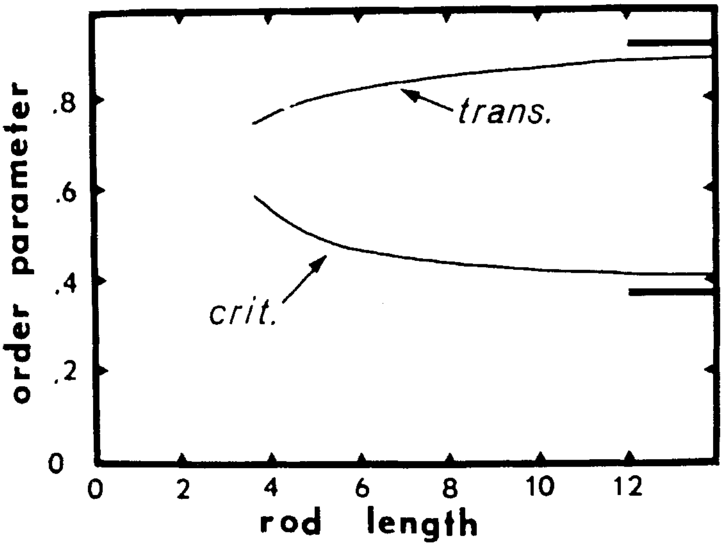

Figure 1. Order parameter at transition and critical points in approximate solution for simple cubic lattice model as function of rod length.[20] The shortest rod for which a stable ordered phase can occur is $X = 3.652$, but a locally stable aligned phase can occur for slightly shorter rods, $X = 3.608$. Longer rods can have locally stable states of greater disorder than shorter ones, $\eta_{\text{crit}} \rightarrow 0.3772$ as $X \rightarrow \infty$. But, the disorder at the transition decreases with increasing rod length, $\eta_{\text{trans}} \rightarrow 0.9149$ as $X \rightarrow \infty$. As described in the text, it is doubtful that these features are present in an exact solution.

more severe packing problems of the disordered state in the original volume.) It is easily seen[4] that

$$\tfrac{1}{2}\beta V(P^{\text{ex}})^2 = \Delta F - \Delta G \tag{12}$$

where V is the volume and β is the compressibility of the disordered state during the expansion. The left hand side of (12) is the " elastic energy of transition ". Since the elastic energy is positive, we see that ΔG is negative when ΔF is zero. Now the system will prefer to remain disordered until ΔG becomes positive. Thus, if we consider some procedure wherein ΔF is steadily increased (compressing the system for example), the transition to an ordered state will occur later than it would have if the elastic energy were zero. When the system finally does order it assumes a state of relatively higher order.

For long rods we find that the excess pressure is large and so the

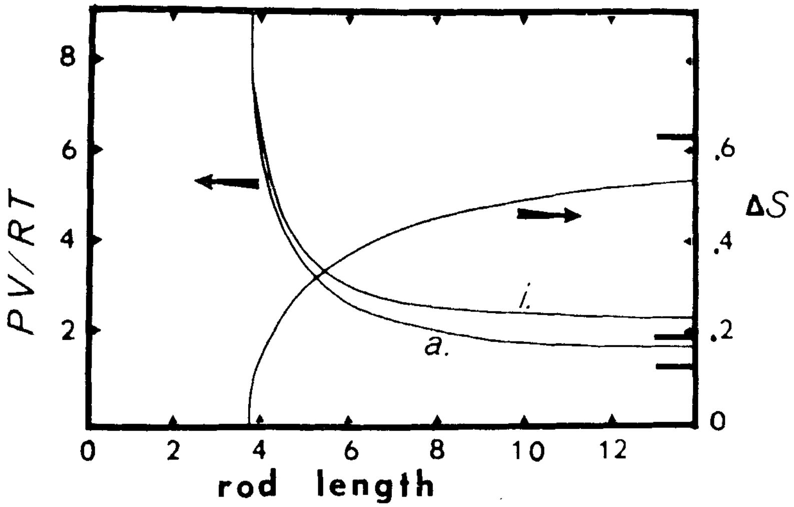

Figure 2. Pressure × Volume/R × Temperature for both isotropic and anisotropic phases at the transition in athermal lattice model. Curve "a" refers to the anisotropic phase and corresponds to smaller volume at the transition than the isotropic phase, curve "i". (Of course, P and T are the same for coexisting phases). The difference between " a " and " i " equals the entropy change ΔS at the transition in this " athermal " model. ΔS is zero for the shortest rods because the elastic energy vanishes as the pressure diverges.

elastic energy is large and the transition takes place with a large volume change and at a high value of η.[G] Now our approximation is such that the entropy of disordered states of long rods is severely underestimated and the excess pressure is more overestimated than in any other case. If for an exact solution the behavior of $\Delta V/V$ with rod length were very different, as it well might be, there would be no reason to expect the behavior of η_{trans} shown in Fig. 1 to be preserved.

In Fig. 2 we show PV/RT and ΔS_{trans} as a function of rod length. The difference of PV/RT from one is a measure of the extent to which rods interfere and is thus a measure of the *effective* density at the transition. The actual transition density f_{trans} is 1 for $X = 3.652$ and decreases as $1/X$ for very long rods.

The case of very long rods is of special interest since it bears some comparison with Zwanzig's(18) virial expansion for long mutually perpendicular parallelpipeds in space. Equations (8), (10) and (11) reduce in the limit $X \to \infty$ to relations among the corresponding state variables,

$$f^* = Xf$$

$$P^* = \frac{XPV_0}{RT} \tag{13}$$

where as before V_0 is the dense molar volume of the rods. For example, η and f^* as well as G/RT are functions of P^*. The transition and " critical " values of the corresponding state variables are given in Table 1. Zwanzig's virial expansion, if it converged well, would provide a much better result than Flory's approximation in cases involving long rods. Unfortunately, the convergence is not very good for the properties which may be compared to our lattice model. In the second part of Table 1 we give η and the ratio of the volumes of the phases for various orders of Zwanzig's virial expansion.(18) We would expect the exact solution to have a volume ratio much closer to 1 than our result. Some tendency for this seems to be present in the virial expansion. It would be of interest to attempt a

TABLE 1 Transition and Critical Parameters for Infinitely Long Rods for the Lattice Model; Comparison with Virial Expansion for Parallelepipeds

Lattice Model	Transition	Critical
η	0.9150	0.3772
$V_{(\text{iso})}/V_{(\text{aniso})}$	1.523	1.130
P^*	4.627	4.399
$f^*_{(\text{iso})}$	2.516	2.430
$f^*_{(\text{aniso})}$	3.831	2.746
$PV/RT_{(\text{iso})}$	1.839	1.810
$PV/RT_{(\text{aniso})}$	1.208	1.602

Virial Expansion—nth approximation

n	= 1	3	4	5	6
(transition)					
η	=0.91	0.94	0.89	0.19	0.70
$V_{(\text{iso})}/V_{(\text{aniso})}$	1.523	1.507	1.404	1.014	1.236

It is expected that the approximate lattice model solution overestimates η_{trans} and the volume change at the transition. The virial expansion result of Zwanzig(18) does not converge well but may bear this out. It is not known if there is any significance to the correspondence between the lattice and first virial expansion results.

virial expansion for the lattice model itself, but this has not yet been reported. Note the peculiar coincidence between first virial expansion results and those for the lattice model.

Flory's results(17) for the lattice model gave the transition value of the order as decreasing with X and tending toward a value equivalent to $\eta = 0.71$. The transition volume ratio increased with rod length (as does ours) and seemed to approach 1.557 (Flory did not actually obtain the asymptotic solution as $X \rightarrow \infty$).

" Athermal " Lattice Model

Next we illustrate features of the transition for a case corresponding to a rod length of 3.85, a pressure of 1250 atm and $V_0 = 200$ cm^3. In Fig. 3 we show the variation of the order parameter with temperature. We have chosen a short rod so that the transition might occur as close as possible to the " critical " temperature. Even so, it is clear that η does not begin to change rapidly until after the transition.

In Fig. 4 we show the isobaric expansivity α as a function of temperature. The fractional transition volume change is equivalent

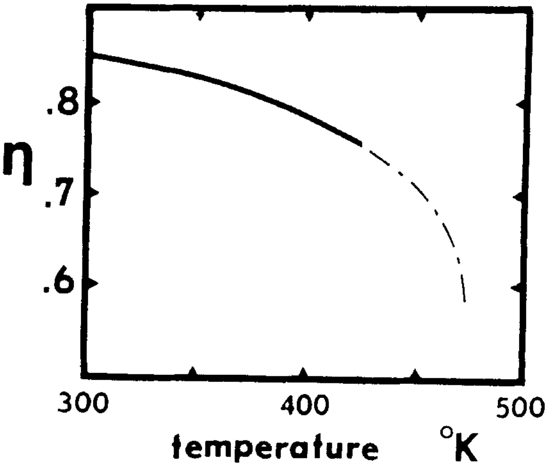

Figure 3. Variation of order parameter with temperature for the athermal lattice model. The heavy line applies to the region for which the ordered phase is stable. The dashed line applies above the transition but before the critical point. The transition occurs well outside the critical " region " of rapid variation of η. For this pressure of 1250 atm we have $T_{\text{trans}} = 424$ °K, $T_{\text{crit}} = 466$ °K and $\eta_{\text{trans}} = 0.754$.

to an integrated expansivity and this is indicated by the shaded area. The ordered phase expansivity diverges at the " critical " temperature, but as expected from Fig. 1, shows little hint of this before the transition.[H] The enhancement of the expansivity in the ordered phase is associated with the fact that as the liquid expands it also becomes less ordered, creating yet a greater need for expansion to alleviate the now intensified packing problem of the more disordered rods.

The coexistence curve in the *P–T* plane is trivial in this athermal model as it corresponds to a curve of constant *P*/*T*. The volume of the phases, the order parameter and many other features are functions of *P*/*T* and so do not change when the transition takes place at higher or lower pressures.

In Fig. 5 we show the normalized *P–V* curve for this same case. Because of the athermal nature of the model this curve applies to all temperatures. Note that at the " critical " temperature, the curve for the anisotropic phase has zero slope, implying the divergent expansivity seen in Fig. 4.

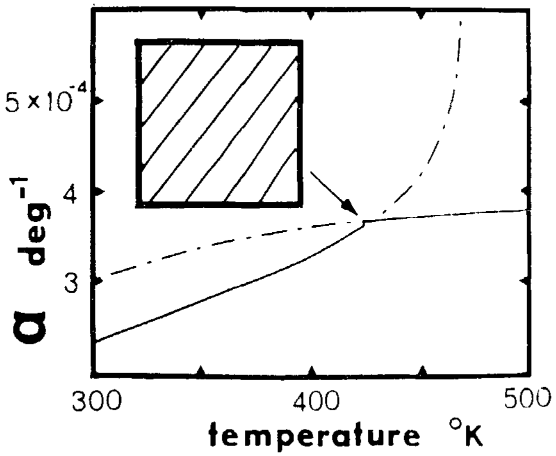

Figure 4. Isobaric expansivity for the athermal lattice model. The equilibrium phase is indicated by the solid line, the locally stable phase by the dashed line. The ordered phase is the equilibrium phase below the transition. The fractional volume change at the transition $(\Delta V/V)|_{\text{trans}}$ is equivalent to an integrated expansivity and is indicated by the shaded area. $(\Delta V/V)|_{\text{trans}} = 0.157$.

VAN DER WAAL'S LATTICE MODEL

The athermal lattice model may be embellished in many ways. We describe now the effect of including an interaction between neighboring filled sites. The purpose of this is to give the model liquid-like as well as gas-like states. We treat the interaction energy in a mean field approximation; that is, we assume that all correlation functions at a given density are unaffected by the interactions.

The principal effect of the attractive energy is to supply a " Van der Waals " internal pressure which varies as the square of the density. There is also, however, a subtle dependence of the mean field energy on the state of order. The origin of this may be most easily seen by considering just two rods in a lattice. If the rods are perpendicular, there are $(4X+2X^2)$ positions in which one rod may be placed so that it touches the other (assumed fixed). There will be one nearest neighbor contact in each position, and so, the average mean field energy is proportional to $(4X+2X^2)$. For two parallel rods, most touching positions represent several contacts. The

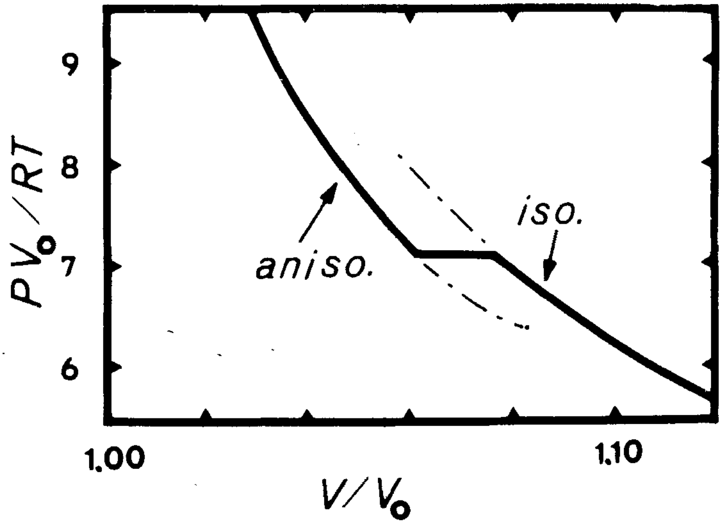

Figure 5. Normalized P–V curve for isotropic and anisotropic phases for the athermal lattice model. The solid line corresponds to the equilibrium state, the dashed lines to locally stable states. V_0 is the volume of one mole at unit density fraction.

average mean field energy turns out to be proportional to $(2+4X^2)$ in this case. Thus, for any rod length greater than one, the mean field energy favors parallel rods. It is generally true that ordered rods have somewhat more ways of touching at a given density than do disordered ones. The effect is slight at high densities and probably would be overwhelmed by genuine correlation effects in a more exact solution, but it does represent a somewhat novel ordering mechanism. The complete result for the mean field energy is:

$$E = WNf\left[\frac{X(\alpha_3/X+1-\alpha_3)^2}{1-(1-1/X)f\alpha_3}\right.$$
$$\left. + \frac{\frac{1}{2}(1-\alpha_3)^2(X+2+1/X)+2\alpha_3(1-\alpha_3)(X+1)+2X^2\alpha_3}{1-\frac{1}{2}(1-1/X)\,f(1-\alpha_3)}\right] \quad (14)$$

where W is the energy for each *pair* of occupied neighbors

In Fig. 6 we present results for α for a model where $X = 3.85$, $W = -295$ R deg/mole and $P = 1$ atm. We show results only for the ordered and disordered liquid-like phases although, for these parameters, the ordered liquid will boil to a gas-like disordered phase before the transition between liquid phases.[1] The transition is even less " critical " here than for the athermal model because the equation of state is such that the elastic energy is very large. The disordering transition takes place from a more highly ordered state than before ($\eta_{\text{trans}} = 0.841$) and with a greater volume change ($\Delta V/V = 0.0198$).

Because the ordering interactions in this model are almost purely steric the coexistence curve is almost an isochore. A measure of the relative sensitivity of the transition to changes in volume and temperature is provided by the quantity $((T/V)\ (\partial V/\partial T))\,|_{\text{trans}}$ for the anisotropic phase. (This is computed by taking differences of results for $P = 1$ and 10 atm.) For this model the value is -0.001 where the decrease in transition volume occurs because the small ordering effect of energy decreases with temperature. The volume must then decrease so as to enhance the contribution of the packing entropy. An opposing tendency exists because of a subtle decrease in the importance of elastic energy at high temperature. The coexistence curve is given by $(\partial T/\partial P)\,|_{\text{trans}} = 103\,^\circ$K/kilobar, where only slight

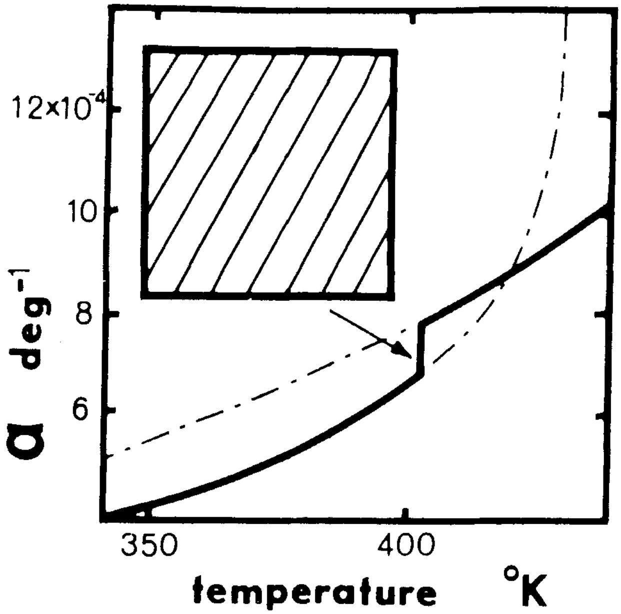

Figure 6. Expansivity in liquid-like state of Van der Waals lattice model. The elastic energy of transition is relatively greater here than for the athermal model because of the difference in the equation of state. The parameters for this model are $X = 3.85$, $W = -285$ R/mole, $P = 1$ atm. and $V_0 = 60$ cm^3.

changes in slope occur at high pressures. The curvature of the coexistence curve is more associated with the equation of state than the transition itself and will not be discussed.

The full details of the coexistence curve are somewhat complicated by the transition line between liquid and gaseous state.(28) As already noted, at low pressure the system boils in the ordered state. At higher pressure the transition is from ordered to disordered liquid and then to the gas. An interesting possibility would occur for longer rods where the ordered liquid might boil to an ordered gas at sufficiently high pressure. (Recall that the ordered states of the athermal model are gas-like.) The liquid vapor critical point would occur in the ordered state and there would be substantial interactions between density changes and those in order. This is one, somewhat indirect, way to create a critical orientation-related phase transition. A more relevant, but also indirect, critical orientational transition would occur at solute points of liquid crystal mixtues.(28,29) There are other possibilities for imbedding the orientational transition in a background which itself undergoes a phase transition. For example, the coupling of orientational " melting "(30) to ordinary melting has been treated by Amzel.(31) (Wulf and DeRocco's(21) work also bears on this.[J]) Suggestions for truely orientational critical transitions have usually invoked a field which couples to the order parameter.(32,33)

The lattice models are greatly idealized systems. Their calculated properties are not surprisingly very different from those of real materials. In the next section we construct models whose basic behavior is more familiar, and which allow us to comprehend better those shortcomings of the theories which are associated with the neglect of short-range-order.

4. Continuum Models

We now apply the ideas developed in the previous section to models of rods in continuous space. We treat four cases: hard rods, rods with isotropic attractive energies, hard rods with both isotropic and anisotropic energies and finally spheres with isotropic and anisotropic energies. The last case is formally identical to a version of Maier and Saupe's(4) phenomenological theory and is used to compare that theory and ours.

HARD RODS

Problems involving the packing of objects in continuous space are basically very complicated. Even spheres, which correspond to the trivial limit of point-rods in the lattice model, cannot be treated exactly.(34) For anisotropic bodies, progress thus far has been very limited.(35) Some of the difficulty, however, does not relate particularly to the orientational phase transition, but rather bears on " background " behavior of the fluid. The salient approximation we will use to account for the distribution of orientations of the rods is really no more serious than for the lattice model (although, as there, it is quite serious).[K] We will use a model which, by choice of the isotropic molecular attraction and the molecular volume, can be made to represent well the background behavior of an organic liquid over the limited range of pressure and temperature for which the phase transition is experimentally accessible. Potential energies are all treated in the mean field approximation. Kinetic energy will be ignored.[L] The crux of the problem then becomes the computation of the orientation-dependent configurational entropy.

The configurational entropy of N rods $N\alpha(\Omega_i)\Delta\Omega$ of which point within $\Delta\Omega$ of the directions Ω_i is:

$$S^c = k\left[\log\left(\frac{\Delta\Omega}{4\pi}\right)^N + \frac{\log N!}{\Pi_i(N\alpha(\Omega_i)\Delta\Omega)!} + \log\left(\frac{\int d\tau'}{N!}\right)\right] \tag{16}$$

where $\int d\tau'$ runs over all configurations such that no two rods overlap and the product over i runs over all orientation directions. The first term in parenthesis insures that S^c remains finite in the limit that the $\Delta\Omega$'s become infinitesimally small. As in the case of (1) and (7), the two terms in (16) may be divided into an entropy of mixing and an entropy of packing. In the limit of large N the mixing term may be written

$$S^{\text{mix}} = -Nk\int \alpha \log 4\pi\alpha \, d\Omega. \tag{17}$$

S^{mix} is a maximum when α is a constant $(1/4\pi)$. As before, S^{mix} favors orientational disorder.

The packing entropy will be estimated by a procedure similar in spirit to that used for the lattice model. We insert rods successively into the volume, count the ways in which a reference point can be accommodated and then reduce this by the probability that the rest of the rod can be built up without interfering with rods already present. As before local order among rods already present is not considered and so, particularly for disordered states and long rods, the ways of placement are severely underestimated (see Sec. 2).

We now compute the packing entropy contribution upon adding a rod. The rods are taken to be cylinders of length l and diameter a terminated by hemispherical endcaps. There are n rods already present and the $(n+1)$st is to point in direction i. The volume accessible to a reference point is just the unoccupied volume $V - nb_0$ where b_0 is the volume of a rod. ($b_0 = \pi a^2 l/4 + \pi a^3/6$.) We next multiply successively by the probabilities that, (1) a bubble of diameter a about the reference point may be created, and (2) that this bubble may be propagated a distance l in the direction i, all without encountering another particle. The processes will succeed if the reference points on each and every rod already present are excluded from a certain volume b^{ex}. If we say that the total available volume is V', the probability that none of n *completely uncorrelated* rods falls in b^{ex} is

$$\left(1-\frac{b^{\mathrm{ex}}}{V'}\right)^n = \exp -\frac{nb^{\mathrm{ex}}}{V'}. \tag{18}$$

For step 1, b^{ex} is readily seen to be:

$$b_1^{\mathrm{ex}} = \frac{3\pi a^2 l}{4} + \frac{7}{6}\pi a^3 \tag{19}$$

where we have accounted for the fact that by definition the center of the bubble does not overlap a rod. This excluded volume is independent of direction.

For step 2 we must consider the relative orientation of rods. In order that a rod may be successfully built out in direction i, the volume excluded to j-direct rods is: (i) the collision cross-section of a sphere travelling in Ω_i with a rod pointing in Ω_j, (ii) multiplied by l. Thus

$$b_2^{\mathrm{ex}}(\theta_{ij}) = (\pi a^2 + 2al\,|\sin\theta_{ij}|)\,l \sim (\pi a^2 + 2al\sin^2\theta_{ij})\,l \tag{20}$$

where θ_{ij} is the angle between Ω_i and Ω_j. The approximation of $|\sin\theta_{ij}|$ by $\sin^2\theta_{ij}$ is mostly accounted for by a slight reinterpretation of the meaning of l; and does simplify later computations. The important feature is the fact that the mutual excluded volume is least for parallel rods and greatest for perpendicular ones. To get the average mutual excluded volume $\overline{b_2^{\mathrm{ex}}}$, we average (20) over the distribution of rods present and that of rods to be added. We add the rods in such an order that these distributions are the same, and arrive at the result:

$$\begin{aligned}\langle\sin^2\theta_{ij}\rangle &= 1-\langle[\cos\theta_i\cos\theta_j+\sin\theta_i\sin\theta_j(\cos\phi_i\cos\phi_j\\ &\qquad +\sin\phi_i\sin\phi_j)]^2\rangle\\ &= \tfrac{2}{3}[1-\eta^2]\end{aligned} \tag{21}$$

where $\eta = \frac{3}{2}(\langle\cos^2\theta\rangle - \frac{1}{3})$ is a measure of the eccentricity of the orientational distribution function. The distribution function itself remains unspecified save that we take it to be cylindrically symmetric about the z-axis. We then have

$$\overline{b_2^{\mathrm{ex}}} = \pi a^2 l\left[1+\frac{4l}{3\pi a}(1-\eta^2)\right]. \tag{22}$$

Clearly the average excluded volume is least when $\eta = 1$ and the system is fully orientationally ordered.

To specify the probability that the rod can be built up now requires an estimate of V' the available volume. If the rods present were really uncorrelated V' would be the same as V, the volume of the container. We can account for some of the *position* correlation introduced by the fact that rods cannot overlap by reducing the available volume to:

$$V' = V - nb_0. \tag{23}$$

Equation (23) is just a convenient way to get a reasonable equation of state. We do not justify it since it bears little on the form of the transition. The salient approximation, which is quite severe, is the neglect of orientational correlation among rods already present. Unfortunately, as for the lattice model this last approximation is difficult to avoid and we make no attempt to improve upon it in this paper.

The result for the probability that the $(n+1)$st rod can be entered is

$$\exp - \frac{n}{V - nb_0}(b_1^{\text{ex}} + \overline{b_2^{\text{ex}}})(\eta). \tag{24}$$

The total configurational entropy, obtained by adding contributions from the steps in S^{pack} for all N rods and then including S^{mix} is given by:

$$\frac{S^c}{Nk} = -\int \alpha \log 4\pi\alpha + \log b_0 + \log\left(\frac{1}{f} - 1\right) - \frac{1}{f}\log(1-f)$$
$$- \left(-\frac{1}{f}\log(1-f) - 1\right)\left(\frac{b_1^{\text{ex}}}{b_0} + \frac{\overline{b_2^{\text{ex}}(\eta)}}{b_0}\right) \tag{25}$$

where $f = Nb_0/V$ is a dimensionless density.

For this case of pure hard core interactions, the Helmholtz free energy is $-TS^c$. As in Sec. 3, we find the distribution and the density which minimizes G at constant T and p by examining all distributions which minimize F at constant f. Now it happens [because of our approximation in (20)] that (25) is of such form that the minimizing distribution function can be found exactly by functional variation. The straight-forward result is

$$\alpha(\theta) = \text{const} \exp(\gamma \cos^2\theta), \tag{26}$$

where γ may be determined from a self consistency requirement on η, or by direct maximation (against a *parameter* as opposed to a function) of (25). The final distribution may be specified entirely in terms of the order parameter η [see (22)].

The nature of the solution is similar to that for the lattice model and also similar to that for various molecular field models (see Refs. (32), (36), (4) and especially (32)). For low density there is only an $\eta = 0$ (disordered) free energy minimum. For intermediate density there are two minima, one for $\eta = 0$ and one for $\eta > 0$ (ordered).$^{\mathrm{M}}$ For higher density there is only a minimum corresponding to an ordered state. The Gibbs free energy and the pressure are given by:

$$\frac{G}{RT} = \int \alpha \log 4\pi\alpha - \log b_0 - \log\left(\frac{1}{f} - 1\right) + \left(\frac{b_1^{\mathrm{ex}}}{b_0} + \frac{b_2^{\overline{\mathrm{ex}}}(\eta)}{b_0}\right)\frac{f}{1-f}, \tag{27}$$

$$\frac{PV_0}{RT} = -\log(1-f) + \left(\frac{b_1^{\mathrm{ex}}}{b_0} + \frac{b_2^{\overline{\mathrm{ex}}}(\eta)}{b_0}\right)\left[\frac{f}{1-f} + \log(1-f)\right], \tag{28}$$

where only the order parameter corresponding to the lowest G at a given P and T corresponds to a physical state. (To obtain G as a function of P and T it is of course necessary to numerically invert the equation of state as described in the Appendix.)

In Fig. 7 we show the behavior of the order parameter at the transition and at the critical point as a function of dimensionless rod length l/a. ($l/a = 0$ corresponds to spheres.) Note that the prefactor of the order dependent packing term in the entropy increases without limit as $f \to 1$. (Compare Fig. 1.) Thus rods of any length can be made to order at sufficiently high density. The order at the "critical" temperature is independent of rod length. ($\eta_{\mathrm{crit}} = 0.323597$.) The amount of disorder at the transition, however, decreases with rod length. Since the value of η for which $\Delta F = 0$ is a constant ($\eta = 0.429032$); the increase in η is entirely associated with the increasing importance of elastic energy. The more significant the coupling of the volume to the order parameter, the less critical is the transition.

HARD RODS WITH ISOTROPIC ENERGY (STERIC MODEL)

One goal of the continuum model calculations is to imbed the orientational phase transition in realistic (non-transition) background

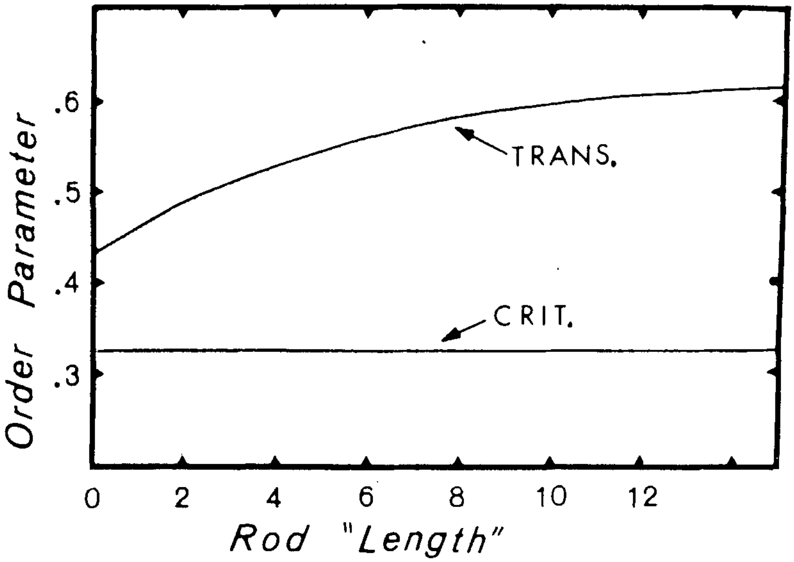

Figure 7. Order parameter at transition and " critical points " in the approximate solution for athermal hard rod models as a function of rod length. Rod " length " is the ratio l/a and is zero for spheres. As l/a approaches zero, the pressure required for an ordered state diverges.

thermodynamics. A fairly good representation of an organic liquid can be gotten by adding an isotropic mean field energy of the form,

$$\frac{E}{N} = -\frac{W_i f}{2}, \tag{29}$$

to the F of the " athermal model ". The solutions then include a Van der Waals liquid-like state in which the transition may take place. For this model W_i was taken as 2.4×10^4 R deg/mole corresponding to an internal pressure of 4000 atm at the typical transition volume of 260 cm^3. V_0 was 200 cm^3 and $l/a = 2$.

In Fig. 8 we show the behavior of expansivity (α), compressibility (β) and specific heat (C) for ordered and disordered liquid-like states. The results are interesting in that, compared to the lattice model, the transition occurs much further into the " critical " region. The factor underlying the pretransition effects is as before the dependence of the volume necessary to accomodate the fluid at a given pressure on the state of order. The behavior of the order parameter is quite similar to that for the " balanced " model (see Fig. 9) to be discussed below.

The coexistence curve for the model reflects the fact that the

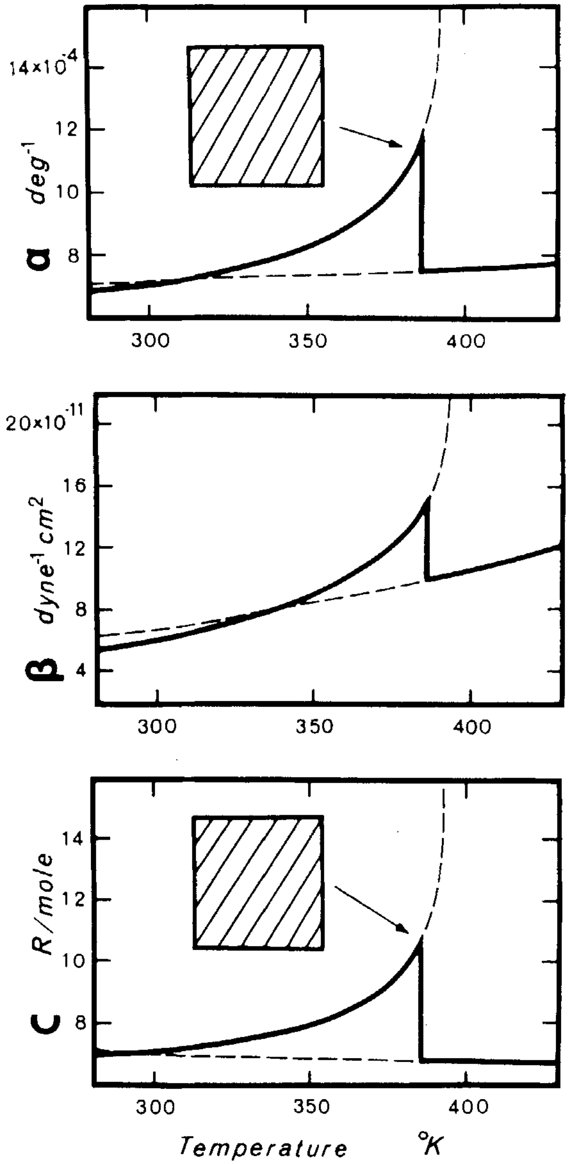

Figure 8. Isobaric expansivity α, isothermal compressibility β, and specific heat at constant pressure C, for hard rod model with isotropic attractive energy (steric model). Results for ordered and disordered liquid-like states are shown. (The disordered gas-like phase is of higher G.) The equilibrium state, indicated by the heavy line, corresponds to the ordered state below and the disordered state above the transition temperature. The dashed line corresponds to locally stable sites. The pressure is 1 atm. $\Delta V/V = 0.0198$ is indicated by the shaded area on the α graph. $\Delta H = 181$ R/mole, the latent heat, is shown by the area on the graph for C. (Compare Fig. 12.)

ordering is determined almost completely by the competition between the "density-dependent" packing entropy and the mixing entropy. Because of the slight dependence of elastic energy on temperature, however, the coexistence curve is not quite an isochore,

$$\left.\frac{T}{V}\frac{\partial V}{\partial T}\right|_{\text{trans}} = 0.0092. \tag{30}$$

Thus the equation of state is affected in such a way that elastic energy becomes less important at high temperature; the system can remain ordered at higher volume. Also the transition value of η decreases slightly at higher temperature:

$$\left.\frac{T\partial\eta}{\partial T}\right|_{\text{trans}} = -0.02. \tag{31}$$

Hard Rod Model with both Isotropic and Anisotropic Energy (Balanced Model)

The close association between density and transition parameters, exemplified by (30) and (31), is a universal property of steric models. It is not observed in experiments. There are a number of modifications which can make our models more realistic in this regard. For example, we might consider temperature-dependent molecular flexibility, used in the description of polymers,$^{(17)}$ which could account for density unrelated thermal effects within a purely steric model. We will not pursue this idea, but rather consider the familiar notion, for liquid crystals, of an orientation-dependent interaction energy$^{(4)}$ among molecules. We introduce this in the usual phenomenological fashion:

$$E_a = -\frac{W_a}{2}\eta^2. \tag{32}$$

This ordering energy is the lowest order term$^{(13)}$ in the moments of the orientation distribution which is consistent with the assumed axial symmetry of the particles and of the distribution.

We next present results for a case in which the role of the ordering energy is to reproduce the experimental balance between the effects of density and of temperature as reflected in the coexistence curve. To simplify the discussion we take the ordering energy as density independent and so account for the effect of density entirely through the packing entropy. (In the next section we discuss density-dependent energies.) The parameters[N] of the model are $l/a = 1.46$, $W_i = 2.2 \times 10^4$ R deg corresponding to an internal pressure of 4200 atm at the transition volume of 152 cm^3 $V_0 = 125$ cm^3 and $W_a = 1509$ R deg.

In Fig. 9 we show the behavior of the order parameter as a function of temperature at 1 atm pressure. The variation becomes rather more rapid before the transition so we would expect to see evidence of pretransition effects.

In Fig. 10 we show curves of constant order parameter in the P–T plane for our model. The coexistence curve corresponds to $\eta = 0.468$ with a slight variation toward lower values at higher pressure. The variation of η along the coexistence curve in this model is as before associated only with changes in the equation of state as they affect the elastic energy. This is because both the energy and packing entropy effects contribute the same η^2 dependence in the free energy and so the mathematical structure of the transition is insensitive to changes in the relative importance of the effects.

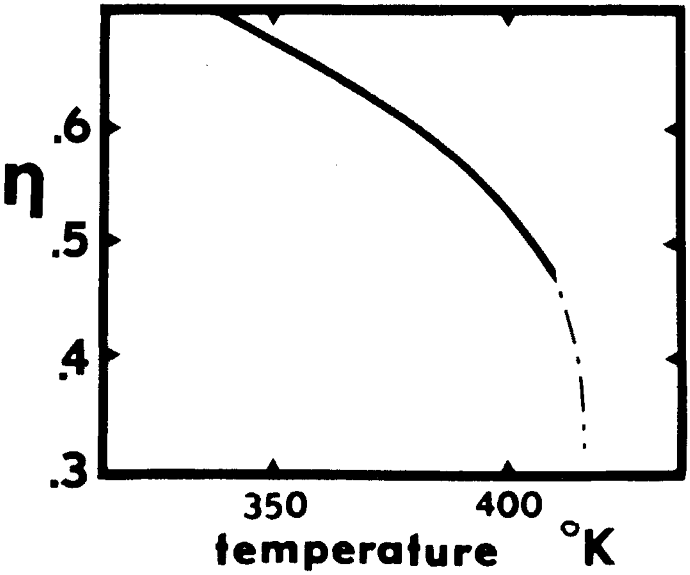

Figure 9. Order parameter vs. temperature for hard rod model with balance of shape and energy effects (balanced model). The region between the transition and " critical " temperatures is shown by the dashed line. Compared with the lattice model (Fig. 3) the transition here occurs much closer to the " critical " region. The pressure is 1 atm.

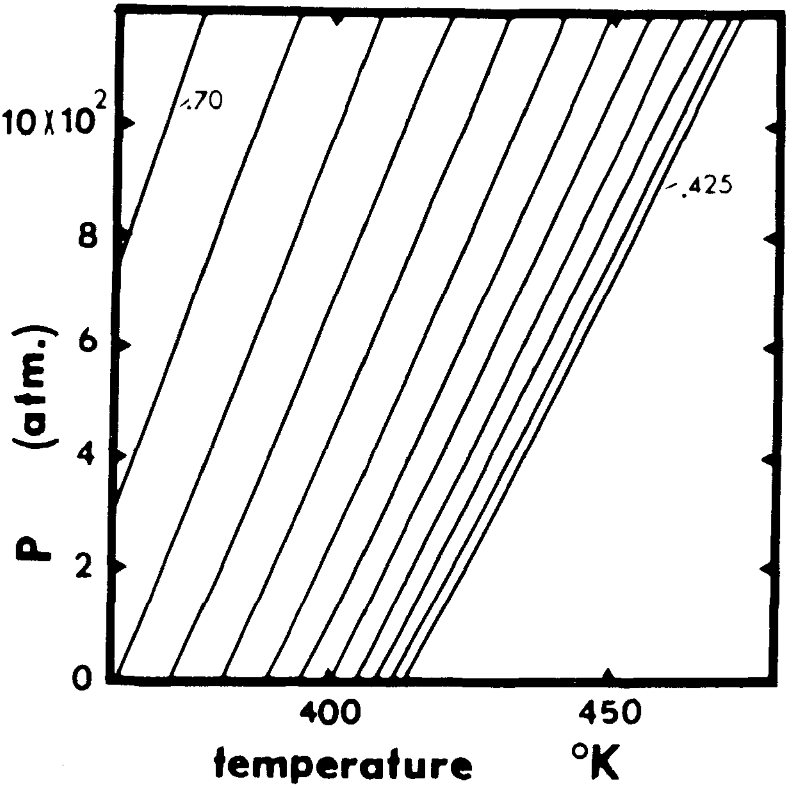

Figure 10. Curves of constant order parameter in the P–T plane for balanced model. The curves correspond to values of η from 0.425 to 0.70 in increments of 0.025. The coexistence curve is approximately $\eta = 0.468$ with η_{trans} decreasing slightly at higher pressures. The curvature is more associated with the equation of state than with the transition itself.

The coexistence curve is not shown in Fig. 10, but its slope is almost the same as the $\eta = 0.475$ and 0.500 lines:

$$\frac{\partial T}{\partial P} = 5.17°/100\,\text{atm}.$$

The relative variation of the volume is given by:

$$\left.\frac{T}{V}\frac{\partial V}{\partial T}\right|_{\text{trans}} = -0.194,$$

and is in magnitude much larger than for the pure hard rod models and incidentally in agreement with experiment (this was of course just due to our choice of parameters$^{\mathrm{N}}$). Because for this model both packing entropy and ordering energy appear in the free energy as coefficients multiplying η^2, it is possible to arrive at a quantitative measure of the relative importance of packing and energy effects. The ratio of packing to energy contributions at the transition point is 1.8. Thus, here packing dominates. We emphasize, however, that this result depends crucially upon the assumed density and temperature dependence of the different effects. Indeed, the coexistence curve can be reproduced by volume-dependent energy effects alone. Thus as we discuss in Sec. 5, this model result does not give definite information on the relative role of packing effects.

In Fig. 11 we present pretransition effects. These are somewhat more " critical " than for the purely steric model because the elastic energy is lower here. The balance between the size of the effects in α, β and C is also different: C is enhanced by a purely " thermal contribution " and α and β are decreased since the variation of effects with density is smaller than for the pure steric case.

SPHERES WITH DENSITY DEPENDENT ANISOTROPIC ENERGY (V^{-2} ENERGY MODEL)

For this last case we employ an isotropic energy, and an ordering energy of the form:

$$E_a = -\frac{W_a V_0^2 \eta^2}{2 \quad V^2}. \tag{33}$$

We neglect the orientation-dependent packing entropy entirely. The non-orientation-dependent " hard sphere " part of the packing provides a background of proper expansivity and compressibility. The parameters are $W_i = 1.86 \times 10^4$ R deg, $W_a = 7312$ R deg, and $V_0 = 97$ cm^3.$^{\mathrm{O}}$

This model is similar to that introduced by Maier and Saupe$^{(4)}$ except that we do not here include their " cluster " parameter (see Sec. 5). Maier and Saupe chose the inverse square volume-dependence since this would follow if the ordering energy were due to anisotropic dispersion forces at long-range and the two particle correlation function scaled with the linear dimensions of the sample. Actually, anisotropic intermolecular forces at short-range are sufficiently complicated$^{(37)}$ that very little is known about the variation with density of the order-dependent energy.

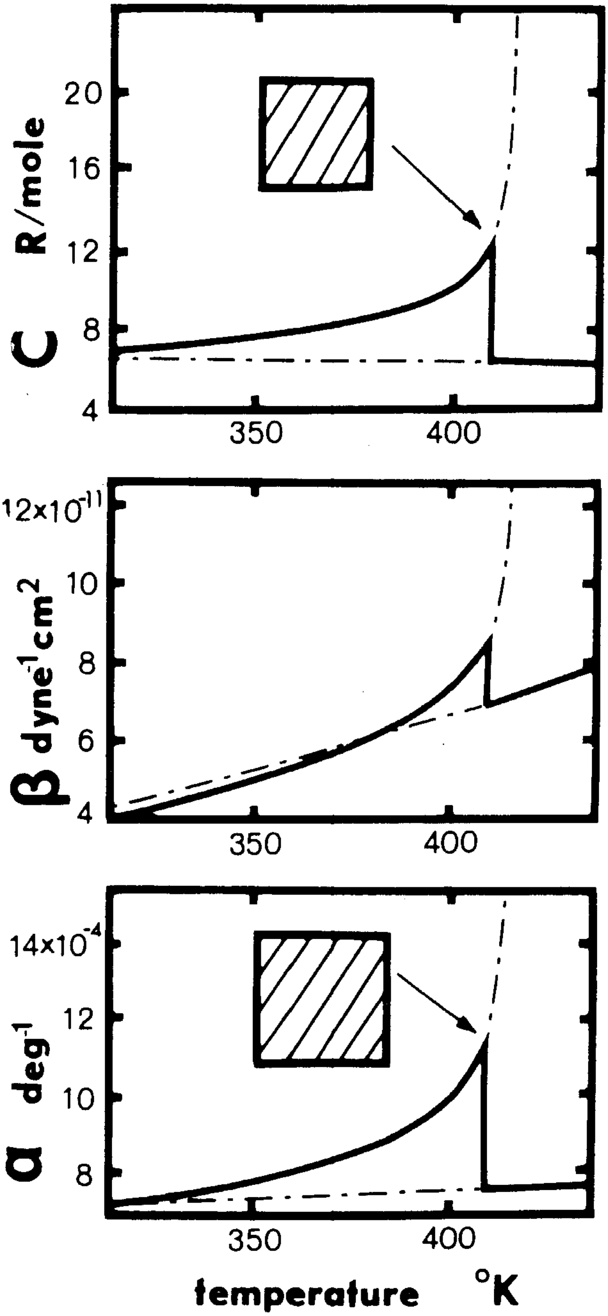

Figure 11. Thermodynamic compliances for balanced model. Compare with Figs. 8 and 12.

The order parameter in the model is determined by the relative sizes of the ordering energy and the mixing entropy and so is a function of TV^2. Thus lines of constant order are characterized by:

$$\left.\frac{T}{V}\frac{\partial V}{\partial T}\right|_{\eta} = -\tfrac{1}{2}. \tag{34}$$

The coexistence curve is given by

$$\left.\frac{T}{V}\frac{\partial V}{\partial T}\right|_{\text{trans}} = -0.42. \tag{35}$$

The difference between (34) and (35) is accounted for by the changing effect of elastic energy. This is reflected in the variation of η along the coexistence curve:

$$\left.\frac{T\,\partial\eta}{\partial T}\right|_{\text{trans}} = -0.44. \tag{36}$$

The order parameter at the transition is 0.494 at 1 atm.

5. Comparison with Experiment

We have avoided comparisons with experiment during the previous discussion in order that the approximate solutions for the models could be presented for what they are. They are not, as we shall now illustrate, good representations of many features of the nematic–isotropic liquid phase transition. It is not difficult to ameliorate matters somewhat by judicious use of phenomenological parameters. However, it seems that short-range-order has a significant role below the transition and that this cannot be well described by long-range-order theories. The discussion will concentrate on static thermodynamic properties, but some mention will also be made of direct measurements of order parameter and their relation to our calculations.

Some experimental results(1,2,4,38,39) for pretransition effects in the well-studied liquid crystal *p*-azoxyanisole (PAA) are shown in Fig. 12 and in Table 2, line (a). A comparison with the results for several continuum models is given in Table 2, lines (b–f) (also see Fig. 10). The properties we discuss are (from left to right in Table 2): discontinuities in volume and enthalpy, total of pretransition and transition volume changes from ordered to disordered state,[P]

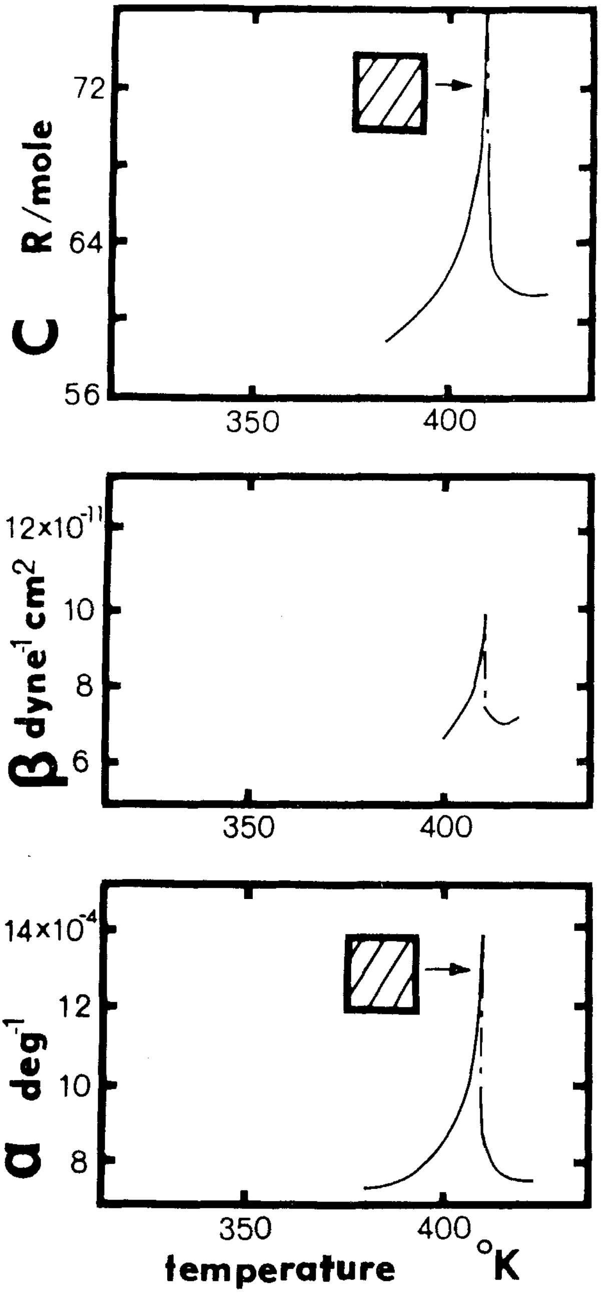

Figure 12. Experimental measurements of pretransition effects in α, β and C for *p*-azoxyanisole. (From Refs. 4, 2 and 1.) Experimental errors are not indicated. Small errors in the assignment of discontinuities could contribute mightily to the pretransition effects, but there is a certain consistency(40) in these very different measurements which lends credibility to them. Compared with an appropriate theoretical model, here the discontinuities $\Delta V/V$ and ΔH are very small (shaded area on α and C graphs). Also the pretransition effects are steeper than predicted by long-range-order theories. Discontinuities in pretransition effects are shown by the dashed line.

TABLE 2 Summary of Transition Properties—Comparison with Experiment

	$\frac{\Delta V}{V}$	ΔH (R deg)	$\left.\frac{\Delta V}{V}\right\|_{\text{total}}$	$\Delta\alpha \times 10^4$ (deg^{-1})	$\Delta\beta \times 10^{11}$ (dyne^{-1} cm^2)	$\frac{\Delta C}{TV} \times 10^4$ R deg^{-1} cm^{-3}	$\frac{T}{V}\frac{\partial V}{\partial T}$	η
Experiment								
(a) PAA	0.0035	68	0.0050	6.2	3.0	1.90	−0.21	0.45
Basic Models								
(b) Steric	0.0186	171	0.0212	4.5	2.7	0.43	+0.01	0.512
(c) Balanced	0.0119	172	0.0151	4.1	1.8	0.99	−0.20	0.467
(d) V^{-2} energy	0.0190	269	0.0257	9.7	2.0	4.04	−0.48	0.494
Cluster—m								
(e) V^{-2} with $m = 4.5$	0.0037	66	0.0049	2.6	0.7	0.95	−0.42	0.444
(f) V^{-4} with $m = 10$	0.0034	44	0.0054	3.3	1.5	0.84	−0.24	0.456

$\left.\frac{\Delta V}{V}\right|_{\text{total}}$ is a sum of transition and pretransition contributions. All other quantities refer to the ordered phase just before the transition or to the transition itself.

line (a)—experimental results from ref. 1, 2, 4, 9 and 39.

lines (b–d)—models from Section IV. Note that $\frac{\Delta V}{V}$ and H are too large. Also $\left|\frac{T}{V}\frac{\partial V}{\partial T}\right|$ is small for the steric model, large for the V^{-2} energy model and just right for the balanced model.

lines (e–f)—models with an extra free parameter to account for short-range-order by assuming clusters of m entities V^{-4} energy has the proper $\frac{T}{V}\frac{\partial V}{\partial T}$ and so also the proper balance among $\Delta\alpha$, $\Delta\beta$ and $\frac{\Delta C}{TV}$. Overall agreement with (a) however is still not good.

departure of α, β and C/TV from their "normal values" at the transition, relative variation of V and T along the coexistence curve, and the value of the order parameter at the transition (η_{trans}). Some of the quantities occur in combinations which make them less sensitive to the fact that the volume of the models, although not far from that of real materials, was not fitted$^{\text{N}}$ and so was not quite correct.

Perhaps the most serious disagreement for the "basic" models (lines b–d) concerns the overestimate of $\Delta V/V$ and ΔH. It is not merely that the distribution of changes between transition and pretransition effects is in error, the total changes are too high by a factor of about three. This means that the influence of the phase transition on the liquid is too strong. The trouble cannot be met by reducing the size of packing or energetic terms for then the ordered state would not be favored. Rather, the transition as a whole is being diluted.

One formal way to reduce the effect of the transition is the cluster concept of Maier and Saupe.(4) Here the short-range-order is assumed to have the effect of creating clusters of molecules such that intra-cluster-order does not change during the transition. S^{mix} is reduced because fewer entities can be disordered and thus less packing entropy or ordering energy is needed to produce an ordered state at a given volume and temperature. The effect of a change in long-range-order on the fluid as a whole is correspondingly reduced. Maier and Saupe originally introduced the cluster parameter to fit their assumed V^{-2} ordering energy theory to their measurements of $\Delta V/V$. As shown in line e, a cluster factor of 4.5 is about right for this purpose. One of the shortcomings which remains concerns the coexistence curve. $((-T/V)(\partial V/\partial T))\,|_{\text{trans}}$ implied by the V^{-2} form of the ordering energy is too large. Clearly some mixing in of hard core effects could be used to reproduce the experimental value. We have rather calculated a case corresponding to an ordering energy which varies as V^{-4} (line f). This fits the coexistence curve and, not surprisingly,(40) gives the proper balance between thermal and pressure-related effects in all properties. The discrepancy which remains, even with the extra free parameter for clustering, concerns the pretransition effects in α, β and C.

The cluster parameter reduces the entire effect of the transition and the pretransition increases in the thermodynamic compliances are very much affected. The reduction for these is less than might be expected since the reduction of the elastic energy of transition allows the system to remain ordered farther into the critical region, and also because the rate of change of the balance between ordering and mixing terms with temperature is quite rapid for the strongly volume-dependent model. Still, the pretransition effects are a factor of two too small. It is to be emphasized that the discrepancy is in the assumed mathematical structure of the transition and not in the choice of parameters[Q] or physical mechanisms. Inclusion of other than η^2 terms in the energy probably could allow for a more critical transition and a better fit. However, experimental results indicate that the long-range-order parameter is quite substantial at the transition and not very much more " critical " than the theories given here predict. This leads to the conclusion that the sorts of long-range-order theories discussed here do not well describe pretransition effects. This last conclusion is opposite to that reached by Chandrasekhar.[R]

In addition to the pretransition effects mentioned here, there is a rapidly expanding literature on measurements more directly measuring the state of order of liquid crystals.(41,42,26) Some of these relate directly to the increasing short-range-order in the isotropic phase which has been completely left out of this theory and which we will not discuss. Of more relevance to this work are reports of the value of order parameter in the ordered phase. The variation of η actually agrees very well with the model calculations for many materials, especially when the overestimate of elastic energy is remedied in some way (use of a cluster parameter, for example). See Table 2 for comparison for PAA. Of note is the fact that for different materials(39) the value of η is often quite different at corresponding temperature distances from the transition. The cause of this is not to be explained by elastic energy, so badly estimated by our theories. Rather, higher-order-than-quadrupolar orienting terms, left out of our theory, are probably responsible. They can be included and apparently can give good agreement(13) on this point. The changing importance of these higher order terms is also a mechanism for variation of η_{trans} with pressure in the same material. (No measurements on this have yet been reported.) Finally, we note that X-ray measurements(25) may be interpreted to yield the angular distribution of molecular axes. Results are consistent with the $e^{+\gamma \cos^2\theta}$ form used in the models, but it is doubtful that measurements so far reported have been sensitive enough to detect subtle deviations caused by higher order intermolecular interactions.

In conclusion, we have discussed approximate solutions for some models which have served to illustrate various mechanisms which give rise to orientational phase transitions. The results hopefully clarify the relation of long-range orientational order to pretransition effects. However, the results cannot be directly compared to measurements on real materials. The direction for improvement does not appear to lie in the use of complicated orienting mechanisms or phenomenological parameters, but rather in a realistic treatment of short-range-order.

Appendix

The calculations of the properties of model systems reported in this paper were performed as follows. The analytic forms of the partial derivatives of the Helmholtz free energy (F) with respect to order parameter (η) and density fraction (f), were obtained as functions of f, η and T. Then the following two simultaneous transcendental equations

$$\frac{\partial F}{\partial \eta} = 0 \qquad \left(\text{with } \frac{\partial^2 F}{\partial \eta^2} > 0\right),$$

$$\frac{f^2}{V_0}\frac{\partial F}{\partial f} = P$$

were solved numerically yielding values for η and f at the given temperature T and pressure P.

Note that:

$$\left.\frac{\partial G}{\partial \eta}\right|_P = \left.\frac{\partial F}{\partial \eta}\right|_f + \left(\left.\frac{\partial F}{\partial f}\right| \frac{\partial f}{\partial \eta}\right)_P - \left(\frac{P V_0}{f^2}\left.\frac{\partial f}{\partial \eta}\right|_P\right) = \left.\frac{\partial F}{\partial \eta}\right|_f$$

so that our minima in F included all minima in G. The lowest was found by comparing values for G at all local minima. The non-transition background behavior is built into the form of F. Where appropriate we chose our parameters in such a way that the background values of α and β were the same as those estimated for PAA.

We obtained α, β, and C by numerically differentiating with respect to f and T and transforming isochoric coefficients to isobaric ones by the usual thermodynamic identities. This eliminated a possible source of numerical error. Based on reproducibility of results for different initial iteration values, numerical errors are usually 1 part in 10^6 and for no result reported here greater than 1 part in 10^3.

It might be noted that the calculations on the continuum models required certain functions related to " Dawson's Integral ". It was impractical to compute these for each state in the multiple iteration processes; and so, we employed seventh order least-square approximations where RMS error was 1 part in 10^7. This was not a major source of error.

Explanatory Footnotes

A. Examples of models with more orientational freedom are Flory's original rigid rod model(17) and the continuum model of Sec. 3 of this paper. The treatments of Cotter (1969)(20) and Dimarzio(19) formally include many directions but do not allow any amount of disorder.

B. Each cell may be either empty or full and all full cells belong to some rod.

C. Rods of length one and parallel rods reduce to the non-interacting Ising model.

D. To avoid double counting we always build rods out in the positive coordinate directions.

E. It is also necessary to examine the boundary of the allowed domain in $\{\alpha\}$. We have done this and contrary to the statement of Dimarzio(19) there are never any boundary minima. All solutions are given by (8).

F. For anisotropic phases η is always between 0.3772 and 1. There can also be roots for negative η but these are never absolute minima in G and will not be discussed further.

G. This tendency is modified by the changes in ΔF itself with η and X.

H. Long rods have a stronger coupling between order and volume and so the ordered phase expansivity can be much larger than that for the isotropic phase. The pretransition effect however is relatively less dramatic than for short rods.

I. This premature boiling could have been avoided by using higher pressures or different parameters. It did not appear worthwhile to recalculate the results since the possibility of boiling does not affect the formal predictions for the liquid crystal–isotropic liquid transition.

J. Wulf and DeRocco did not concentrate on the behavior of the orientational order at the presumed liquid–solid phase transition. Rather, they felt that the existence of multiple transitions in the presence of orientational order could be used to better demonstrate the fluid nature of the ordered states for the model systems. For models such as Flory's the fluid nature seems implicit in the assumed nature of the correlation functions.

K. The analogy to the 2-site correlation function (2) is not known exactly here. This mostly means that certain " geometrical " parameters which appear in the theory are not so accurately related to the physical dimensions of the model rods. A further difficulty arises because Flory's approximation when applied to non-orthogonal rods, become dependent on the order in which the differently oriented rods are placed into the volume. The structure of the transition is not affected.

L. Translational kinetic energy may be rigorously separated out of the problem. Rotational kinetic energy, however, does present a problem.

M. Local minima occur for $0.323597 < \eta < 1$. As for the lattice model, negative η solutions are never absolute minima.

N. The choice of W_i and V_0 was made such that the expansivity and compressibility of the isotropic phase at about 410° were: $\alpha \sim 7.5 \times 10^4$ and $\beta \sim 6.9 \times 10^{-11}$ and thus close to the values for PAA. l/a and W_a were chosen such that the transition occurred close to 410 °K and the coexistence curve had the proper slope. Thus four features were fitted by choice of four parameters. It is interesting that the molar volume of the model at the transition was not far off from the 225 cm^3 value for PAA. Thus, the " background " thermodynamics were fairly well taken care of.

O. In this model W_i and V_0 were again chosen to fit the expansivity and compressibility of the isotropic phase to realistic values at 410 °K: $\alpha = 7.57 \times 10^{-4}$, $\beta = 6.92 \times 10^{-11}$. W_a was chosen so that T_{trans} was 410 °K. Thus three features were fitted by choice of three parameters. The slope of the coexistence curve was not fitted and does not agree with experiment.

P. This is gotten by the following convention. We add to the discontinuous changes at the transition, the integral of the departure of α or C from " background " values from 10 °K below to 10 °K above the transition.

Q. A broad range of exponents and cluster parameters have been examined.

R. Chandrasekhar(13) used a more general dependence of the energy on the state of order. However, we do not feel that the excellent agreement he obtained for pretransition effects in specific heat in PAA is due to extra parameters. Rather, we feel he has left an inconsistency in his theory. He defines a free energy F_s which depends on the state of order and which is zero in the disordered state. He notes that at the transition the condition, $F_s = -(\partial F_s/\partial V)(\Delta V/2)$, is fulfilled. Apparently he then chooses parameters such that, for the experimental ΔV, the condition is fulfilled at the experimental transition temperature. However, there is another condition on ΔV which comes from consideration of the excess pressure associated with the transition, $\Delta V = -V\beta(\partial F_s/\partial V)$. This will not generally be met by the same parameters which met the first condition. Ignoring the second condition allowed $\Delta V/V$ to be fitted without use of a cluster parameter and also made the theory intrinsically more critical. This approach, however, does not seem legitimate.

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