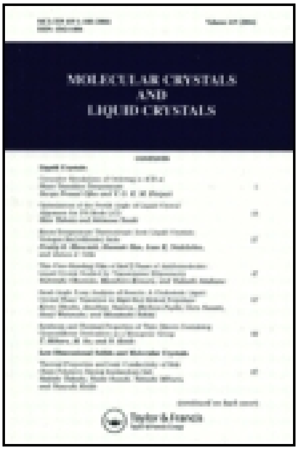

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A Quasi-Chemical Lattice Treatment of Rod-like Molecules. Application to the Nematic-Isotropic Transition

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Abstract—A quasi-chemical treatment is applied to a face-centered cubic lattice system containing N_0 holes (or " solute molecules ") and N_x interacting rods of length-to-breadth ratio x. The resulting partition function is then maximized with respect to the numbers of rods in each of the six allowed directions on the lattice. Two stable " phases " are obtained: a completely aligned " phase ", more stable at lower volume fractions of holes v_0, and an isotropic " phase ", more stable at higher v_0's. When alignment is not favored energetically, the relative stabilities of these two " phases " are temperature independent, but when alignment is favored, this is no longer the case and a first-order aligned → isotropic transition is observed. When the dependencies of the transition temperature and enthalpy of transition on the segment interaction energies of the system, on v_0, and on x are determined, it is found that our simple model is able to predict a number of important aspects of the behavior of nematogenic substances at their nematic-isotropic transitions.

Introduction

The mesomorphic states of matter are highly complex and incompletely understood, making realistic statistical mechanical treatments impossible at present. One can, however, consider various simple models having selected properties in common with mesomorphic systems. (In general, the more sophisticated the model, the more approximate the treatment must be.) With a given model, one can treat only a few specialized aspects of mesomorphic behavior; in fact, the particular aspects to be investigated largely determine the type of model used. Maier and Saupe,[1] for example, in their treatment of molecules dissolved in liquid crystal solvents, incorporated dispersion forces into their model in a detailed manner, but did not consider repulsive forces or the rod-like nature of the solvent molecules, while Ericksen,[2] attempting to explain the mechanical properties of mesophases, used a continuum model which ignores the molecular nature of real systems.

For the purpose of investigating the nematic–isotropic phase transition, lattice systems of rigid rods are particularly useful because they offer the possibility for both isotropic and anisotropic arrangements of the rods, yet can be handled in a straightforward manner.

Flory[3] considered a lattice of holes and long rigid rods (length-to-breadth ratios of the order of 100) with partial orientation about a preferred spatial axis. He looked at both athermal and non-athermal systems and found in both cases that, above a certain concentration of holes, phase separation occurred giving a dilute isotropic phase and a more concentrated anisotropic phase. Both his method of obtaining partial orientation and his treatment of non-athermal systems were highly approximate, however, the former consisting of replacing a molecule inclined at an angle ψ_i to the preferred axis by $x \cdot \sin \psi_i$ submolecules situated on adjacent rows in step fashion, and the latter consisting merely of the addition of a van Laar type term to the partition function for an athermal system. DiMarzio[4] later treated a system of non-interacting rods and holes on a simple cubic lattice, allowing the rods to lie in three mutually orthogonal directions, and obtained two stable phases: a completely aligned phase, more stable at lower volume fractions of holes, and an isotropic phase, more stable at higher volume fractions of holes. The present treatment, however, is the first to consider a system of *interacting* rods in more than a superficial manner. Using a quasi-chemical lattice approach, we investigate the extent to which certain properties of nematogenic substances influence and determine the behavior of their nematic–isotropic transitions.

Lattice Model

Our model consists of a face-centered cubic (fcc) lattice of N sites upon which are placed N_x straight rigid interacting rods, each occupying x sites, and N_0 " solute molecules ", each occupying one site. (Later we shall restrict ourselves to the special case of rods and holes on a lattice, but, for the present, let us make the treatment as general as possible.) Thus,

$$N = N_0 + xN_x. \tag{1}$$

Furthermore, our choice of an fcc lattice fixes the number of nearest neighbors z to each site at 12 and the number of allowed and distinguishable directions in which the rods can lie at 6. The number of rods in the ith direction will be denoted by N_i. Clearly

$$\sum_{i=1}^{6} N_i = N_x \tag{2}$$

Quasi-Chemical Treatment

In order to treat our lattice of interacting species as realistically as possible without incurring intractable mathematical difficulties, we employ the so-called quasi-chemical or Bethe–Guggenheim approximation, the particular formulation used being an extension of the combinatorial method of Hill.[5] Applying this approach necessitates our considering rods in each of the six allowed directions to be formally different species. There are, then, 49 distinguishable ways in which a pair of nearest neighbor sites, represented by $\underline{\quad}\,\underline{\quad}$, can be occupied; namely $\underline{0}\,\underline{0}$, $\underline{0}\,\underline{i}$, $\underline{i}\,\underline{0}$, $\underline{i}\,\underline{i}$, $\underline{i}\,\underline{j}$, and $\underline{j}\,\underline{i}$ ($i = 1, \ldots, 6$; $j = 1, \ldots, 6$; $i \neq j$), where 0 indicates occupation of the site by a " solute molecule " and i and j indicate occupation by a segment of a rod lying in the ith and jth direction, respectively. Of the 49 variables N_{mn} denoting the number of pairs of sites of the type $\underline{m}\,\underline{n}$ ($m = 0, 1, \ldots, 6$; $n = 0, 1, \ldots, 6$), only 42 are independent because of the following relationships:

$$2N_{00} + \sum_{i=1}^{6} (N_{0i} + N_{i0}) = zN_0 \tag{3}$$

$$2N_{ii} + N_{0i} + N_{i0} + \sum_{j \neq i} (N_{ij} + N_{ji}) = qzN_i \quad (i = 1, \ldots, 6)$$

where q is defined by

$$q = (xz - 2x + 2)/z; \tag{4}$$

that is, qz equals the number of nearest neighbor sites to the x sites occupied by a rod excluding those neighbors of each site occupied by an adjoining segment of the same rod. We choose the N_{0i}, N_{i0}, and $N_{ij} (i \neq j)$ as the independent variables and obtain N_{00} and the N_{ii} from (3). In addition, there are four independent segment interaction energies to be considered: w_{00}, the interaction energy between two " solute molecules " on neighboring sites; w_{0x}, the interaction energy between a " solute molecule " and an adjacent segment of a rod lying in any direction; w_{xx}, the interaction energy between neighboring segments of two rods lying in the same direction; and $w_{xx'}$, the interaction energy between neighboring segments of two rods in different directions. $w_{xx'}$ will equal w_{xx} only when alignment of the rods is not favored energetically.

Considering nearest neighbor interactions only, the configurational partition function for the lattice is given by

$$Q_{\text{configurational}} = \sum_{\mathbf{N}_{mn}} g(N_0, \mathbf{N}_i, \mathbf{N}_{mn}) \exp\left[- W(N_0, \mathbf{N}_i, \mathbf{N}_{mn})/(kT) \right] \tag{5}$$

where $\mathbf{N}_i$ represents the set $\{N_1, \ldots, N_6\}$ and $\mathbf{N}_{mn}$ represents the set $\{N_{0i}, N_{i0}, N_{ij};\ i = 1, \ldots, 6, j = 1, \ldots, 6;\ i \neq j\}$. g is the number of ways of placing N_0 " solute molecules " and N_x rods (with N_i rods in the ith direction) on the lattice such that there are N_{01} 01 pairs, N_{10} 10 pairs, ..., N_{65} 65 pairs and W is the total configurational energy of the system for this choice of $\mathbf{N}_{mn}$. In other words, $Q_{\text{configurational}}$ (hereafter denoted by Q_c) is the sum over all possible configurational energy levels for the lattice of the degeneracy of the level multiplied by the appropriate Boltzmann factor. For a three-dimensional lattice of interacting moieties, g cannot be determined exactly and approximate methods must be employed. The essence of the quasi-chemical approximation is that we can treat pairs of neighboring sites as independent in a certain sense, even though we know that, in fact, many such pairs overlap. In the combinatorial approach, we calculate $\omega(N_0, \mathbf{N}_i, \mathbf{N}_{mn})$, the number of ways of randomly arranging N_{01} 01 pairs, N_{10} 10 pairs, ..., N_{65} 65 pairs, assuming complete independence for all pairs, and then assume that g is equal to ω except for a normalization factor C. That is, we assume that

$$g(N_0, \mathbf{N}_i, \mathbf{N}_{mn}) = C(N_0, \mathbf{N}_i)\omega(N_0, \mathbf{N}_i, \mathbf{N}_{mn}). \tag{6}$$

(C will be $\ll 1$ since many physically impossible configurations are counted in ω.) Determination of ω is a standard elementary combinatorial problem. Clearly

$$\omega = \frac{\left(N_{00} + \sum_{i=1}^{6}(N_{0i} + N_{i0}) + \sum_{i=1}^{6} N_{ii} + \sum_{i \neq j} N_{ij}\right)!}{N_{00}! \prod_{i=1}^{6}[N_{0i}!N_{i0}!N_{ii}!] \prod_{i \neq j} N_{ij}!}$$

which, utilizing (3), becomes

$$\omega = \frac{[\tfrac{1}{2}z(N_0 + qN_x]!}{[\tfrac{1}{2}(zN_0 - \sum_{i=1}^{6}(N_{i0} + N_{0i}))]! \prod_{i=1}^{6}\{N_{0i}!N_{i0}![\tfrac{1}{2}(qzN_i - N_{0i} - N_{i0} - \sum_{j \neq i}(N_{ij} + N_{ji}))]!\} \prod_{i \neq j} N_{ij}!} \tag{7}$$

To obtain C, we sum over $\mathbf{N}_{mn}$ in (6):

$$C(N_0, \mathbf{N}_i) \sum_{\mathbf{N}_{mn}} \omega(N_0, \mathbf{N}_i, \mathbf{N}_{mn}) = \sum_{\mathbf{N}_{mn}} g(N_0, \mathbf{N}_i, \mathbf{N}_{mn}) = g(N_0, \mathbf{N}_i), \tag{8}$$

where $g(N_0, \mathbf{N}_i)$ is the number of ways of randomly placing N_0 " solute molecules ", N_1 rods in direction 1, N_2 rods in direction 2, ..., and N_6 rods in direction 6 on the lattice. It is determined readily using the counting method of DiMarzio,[4] who derived the expression (Eq. (7) of his paper)

$$g(N_1, N_2, N_3, N_0) = \frac{\prod_{i=1}^{3}[N - (x-1)N_i]!}{N_0! \prod_{i=1}^{3}[N_i!](N!)^2} \tag{9}$$

for the number of ways of packing N_0 holes and N_x rods onto a simple cubic lattice with N_1 rods in direction 1, N_2 rods in direction 2, and N_3 rods in direction 3. (There are only 3 allowed directions for rods.) This can be extended directly to

$$g(N_0, \mathbf{N}_i) = \frac{\prod_{i=1}^{6} [N - (x - 1)N_i]!}{N_0!(N!)^5 \prod_{i=1}^{6} (N_i!)} \tag{10}$$

for an fcc lattice, even though in this case all the allowed directions for rods are not mutually orthogonal as they are for a simple cubic lattice. Actually, such mutual orthogonality is not needed in order to apply this counting scheme; rather, it is sufficient that the ends of exactly x rods in the jth direction be able to fit along one side of a rod in the ith direction for all i and j—a condition that is satisfied on an fcc lattice. Knowing $g(N_0, \mathbf{N}_i)$, we can find $C(N_0, \mathbf{N}_i)$ from (8). The summation over $\mathbf{N}_{mn}$ cannot be performed, but the sum can be replaced by its maximum term. Thus

$$C \doteq g(N_0, \mathbf{N}_i)/\omega_{\max} \tag{11}$$

or

$$\ln C = \ln g(N_0, \mathbf{N}_i) - \ln \omega_{\max} \tag{12}$$

For the sake of convenience, we maximize $\ln \omega$ rather than ω itself. Using Stirling's approximation,

$$\begin{aligned}\ln \omega = {} & \tfrac{1}{2}z(N_0 + qN_x) \ln [\tfrac{1}{2}z(N_0 + qN_x)] - \tfrac{1}{2}[zN_0 - \sum_{i=1}^{6} (N_{0i} + N_{i0})] \\ & \times \ln [\tfrac{1}{2}(zN_0 - \sum_{i=1}^{6} (N_{0i} + N_{i0}))] - \sum_{i=1}^{6} \{(N_{0i} \ln N_{0i} + N_{i0} \ln N_{i0}) \\ & + \tfrac{1}{2}[qzN_i - N_{0i} - N_{i0} - \sum_{j \neq i} (N_{ij} + N_{ji})] \\ & \times \ln [\tfrac{1}{2}(qzN_i - N_{0i} - N_{i0} - \sum_{j \neq i} (N_{ij} + N_{ji}))]\} - \sum_{i \neq j} N_{ij} \ln N_{ij}.\end{aligned} \tag{13}$$

Maximizing $\ln \omega$ with respect to the set $\mathbf{N}_{mn}$ yields the set of simultaneous equations

$$\frac{4(N'_{0i})^2}{[zN_0 - \sum_{k=1}^{6}(N'_{0k} + N'_{k0})][qzN_i - N'_{0i} - N'_{i0} - \sum_{l \neq i}(N'_{il} + N'_{li})]} = 1 \qquad (i = 1, \ldots, 6)$$

$$\frac{4(N'_{i0})^2}{[zN_0 - \sum_{k=1}^{6}(N'_{0k} + N'_{k0})][qzN_i - N'_{0i} - N'_{i0} - \sum_{l \neq i}(N'_{il} + N'_{li})]} = 1 \qquad (i = 1, \ldots, 6)$$

$$\frac{4(N'_{ij})^2}{[qzN_i - N'_{0i} - N'_{i0} - \sum_{l \neq i}(N'_{il} + N'_{li})][qzN_j - N'_{0j} - N'_{j0} - \sum_{m \neq j}(N'_{jm} + N'_{mj})]} = 1 \qquad \left\{\begin{array}{l} i = 1, \ldots, 6 \\ j = 1, \ldots, 6 \\ i \neq j \end{array}\right\} \qquad (14)$$

where the primes denote those values of the N_{mn} which maximize $\ln \omega$. The solution is

$$N'_{0i} = N'_{i0} = \frac{qzN_0N_i}{2(N_0 + qN_x)} \qquad (i = 1, \ldots, 6)$$

$$N'_{ij} = N'_{ji} = \frac{q^2zN_iN_j}{2(N_0 + qN_x)} \qquad \left\{\begin{array}{l} i = 1, \ldots, 6 \\ j = 1, \ldots, 6 \\ i \neq j \end{array}\right\} \qquad (15)$$

Putting (15) into (13) to obtain $\ln \omega_{\max}$ and then using (12) yields, after simplification,

$$\ln C = \ln g(N_0, \mathbf{N}_i) + zN_0 \ln\left\{\frac{N_0}{N_0 + qN_x}\right\} + \sum_{i=1}^{6} qzN_i \ln\left\{\frac{qN_i}{N_0 + qN_x}\right\} \qquad (16)$$

or

$$C = \frac{\prod_{i=1}^{6} \{[N - (x-1)N_i]!(qN_i)^{qzN_i}\} N_0^{zN_0}}{N_0!(N!)^5 \prod_{i=1}^{6} (N_i!)(N_0 + qN_x)^{z(N_0+qN_x)}} \qquad (17)$$

Utilizing (6), (10), and (17), we can now find $g(N_0, \mathbf{N}_i, \mathbf{N}_{mn})$. Putting this g into (15), replacing the sum over $\mathbf{N}_{mn}$ by its maximum term, and taking the logarithm of Q_c gives

$$\begin{aligned}
\ln Q_c = {} & \sum_{i=1}^{6} [N - (x-1)N_i] \ln [N - (x-1)N_i] - N_0 \ln N_0 \\
& - 5N \ln N - \sum_{i=1}^{6} N_i \ln N_i + \frac{zN_0}{2} \ln \left\{ \frac{zN_0^2}{N_0 + qN_x} \right\} \\
& + \sum_{i=1}^{6} \frac{qzN_i}{2} \ln \left\{ \frac{q^2 zN_i^2}{N_0 + qN_x} \right\} - \sum_{i=1}^{6} (\overline{N}_{0i} \ln \overline{N}_{0i} + \overline{N}_{i0} \ln \overline{N}_{i0}) \\
& - \sum_{i \neq j} \overline{N}_{ij} \ln \overline{N}_{ij} - \frac{1}{2} \left[zN_0 - \sum_{i=1}^{6} (\overline{N}_{0i} + \overline{N}_{i0}) \right] \\
& \times \ln \left\{ \frac{1}{2} \left[zN_0 - \sum_{i=1}^{6} (\overline{N}_{0i} + \overline{N}_{i0}) \right] \right\} - \sum_{i=1}^{6} \Bigg\{ \frac{1}{2} \Bigg[qzN_i - \overline{N}_{0i} - \overline{N}_{i0} \\
& - \sum_{j \neq i} (\overline{N}_{ij} + \overline{N}_{ji}) \Bigg] \Bigg\} \ln \Bigg\{ \frac{1}{2} \Bigg[qzN_i - \overline{N}_{0i} - \overline{N}_{i0} \\
& - \sum_{j = i} (\overline{N}_{ij} + \overline{N}_{ji}) \Bigg] \Bigg\} - \frac{\overline{W}}{kT}
\end{aligned} \tag{18}$$

where the bars indicate those values of the N_{mn} which maximize $\ln Q_c$ (and hence Q_c) and

$$\begin{aligned}
\overline{W} & = \overline{N}_{00} w_{00} + \sum_{i=1}^{6} (\overline{N}_{0i} + \overline{N}_{i0}) w_{0x} + \sum_{i=1}^{6} \overline{N}_{ii} w_{xx} + \sum_{i \neq j} \overline{N}_{ij} w_{xx'} \\
& = \frac{1}{2} \left[zN_0 - \sum_{i=1}^{6} (\overline{N}_{0i} + \overline{N}_{i0}) \right] w_{00} + \sum_{i=1}^{6} (\overline{N}_{0i} + \overline{N}_{i0}) w_{0x} \\
& \quad + \frac{1}{2} \left[qzN_x - \sum_{i=1}^{6} (\overline{N}_{0i} + \overline{N}_{i0}) - 2 \sum_{i \neq j} \overline{N}_{ij} \right] w_{xx} + \sum_{i \neq j} \overline{N}_{ij} w_{xx'}
\end{aligned} \tag{19}$$

Maximizing the quantity $[\ln g(N_0, \mathbf{N}_i, \mathbf{N}_{mn}) - W(N_0, \mathbf{N}_i, \mathbf{N}_{mn})/(kT)]$ with respect to the variables $\mathbf{N}_{mn}$, we obtain

$$\frac{4\overline{N}_{0i}^2}{\left[zN_0 - \sum_{i=1}^{6} (\overline{N}_{0i} + \overline{N}_{i0}) \right] \left[qzN_i - \overline{N}_{0i} - \overline{N}_{i0} - \sum_{l \neq i} (\overline{N}_{il} + \overline{N}_{li}) \right]} = \exp [-2w/(kT)]$$

$$\frac{4\bar{N}_{i0}^2}{\left[zN_0 - \sum_{i=1}^{6}(\bar{N}_{0i} + \bar{N}_{i0})\right]\left[qzN_i - \bar{N}_{0i} - \bar{N}_{i0} - \sum_{l\neq i}(\bar{N}_{il} + \bar{N}_{li})\right]} = \exp\,[-2w/(kT)]$$

$$\frac{4\bar{N}_{ij}^2}{[qzN_i - \bar{N}_{0i} - \bar{N}_{i0} - \sum_{l\neq i}(\bar{N}_{il} + \bar{N}_{li})][qzN_j - \bar{N}_{0j} - \bar{N}_{j0} - \sum_{m\neq j}(\bar{N}_{mj} + \bar{N}_{jm})]} = \exp\,[-2w'/(kT)]$$

$$(i = 1, \ldots, 6;\ j = 1, \ldots, 6;\ i \neq j) \tag{20}$$

where

$$w = w_{0x} - \tfrac{1}{2}(w_{00} + w_{xx}) \tag{21}$$

and

$$w' = w_{xx'} - w_{xx} \tag{22}$$

When $w_{xx'} \neq w_{xx}$, this set of equations cannot be solved in general (for any arbitrary $\mathbf{N}_i$), though it can be solved for various special cases, as will be seen later. When $w_{xx'} = w_{xx}$, the solution is

$$\begin{aligned} \bar{N}_{0i} &= \bar{N}_{i0} = \frac{qzN_0N_i}{N_0 + qN_x + \beta} && (i = 1, \ldots, 6) \\ \bar{N}_{ij} &= \bar{N}_{ji} = \frac{q^2zN_iN_jR}{N_0 + (2R-1)qN_x + \beta} && \left\{\begin{matrix} i = 1, \ldots, 6 \\ j = 1, \ldots, 6 \\ i \neq j \end{matrix}\right\} \end{aligned} \tag{23}$$

where

$$R = \exp\,[2w/(kT)]$$

and

$$\beta = \sqrt{(N_0 - qN_x)^2 + 4RqN_0N_x} \tag{24}$$

Thus far, we have treated the N_i as known quantities. Actually, of course, we wish to choose $\mathbf{N}_i$ so as to maximize $\ln Q_c$ and thereby minimize the free energy of our system. That is, we wish to maximize $\ln Q_c$ with respect to $\{N_1, N_2, \ldots, N_6\}$ under the constraint $\sum_{i=1}^{6} N_i = N_x$. Rather than employing the conventional Lagrange multiplier for this purpose, it is more convenient to substitute $(N_x - \sum_{i=1}^{5} N_i)$ for N_6 and then maximize with respect to

N_1 through N_5 only. After straightforward but lengthy algebra, six sets of solutions are obtained:

1. $N_1 = N_x;\ N_2 = N_3 = N_4 = N_5 = N_6 = 0$
   $N_2 = N_x;\ N_1 = N_3 = N_4 = N_5 = N_6 = 0$
   $\vdots$ (4 more equivalent solutions)

2. $N_1 = N_2 = \frac{1}{2}N_x;\ N_3 = N_4 = N_5 = N_6 = 0$
   $N_1 = N_3 = \frac{1}{2}N_x;\ N_2 = N_4 = N_5 = N_6 = 0$
   $\vdots$ (13 more equivalent solutions)

3. $N_1 = N_2 = N_3 = \frac{1}{3}N_x;\ N_4 = N_5 = N_6 = 0$
   $N_1 = N_2 = N_4 = \frac{1}{3}N_x;\ N_3 = N_5 = N_6 = 0$
   $\vdots$ (18 more equivalent solutions)

4. $N_1 = N_2 = N_3 = N_4 = \frac{1}{4}N_x;\ N_5 = N_6 = 0$
   $N_1 = N_2 = N_3 = N_5 = \frac{1}{4}N_x;\ N_4 = N_6 = 0$
   $\vdots$ (13 more equivalent solutions)

5. $N_1 = N_2 = N_3 = N_4 = N_5 = \frac{1}{5}N_x;\ N_6 = 0$
   $N_1 = N_2 = N_3 = N_4 = N_6 = \frac{1}{5}N_x;\ N_5 = 0$
   $\vdots$ (4 more equivalent solutions)

6. $N_1 = N_2 = N_3 = N_4 = N_5 = N_6 = \frac{1}{6}N_x.$ (25)

When each of these six types of solutions is put into (18), making use of (20), a different expression for $\ln Q_c$ results, as expected. These are given by the general expression

$$\begin{aligned}\ln Q_c^{(n)} &= [nN - (x-1)N_x]\ln[N - (x-1)N_x/n] - N_0 \ln N_0 \\ &\quad - N_x \ln(N_x/n) - (n-1)N\ln N \\ &\quad - \frac{zN_0}{2}\ln\left\{\frac{2R(N_0+qN_x)}{(2R-1)N_0+qN_x+\beta}\right\} - \frac{qzN_x}{2} \\ &\quad \times \ln\left\{\frac{2R(N_0+qN_x)}{N_0+(2R-1)qN_x+\beta}\right\} - \frac{z}{2kT}(N_0w_{00}+qN_xw_{xx})\end{aligned} \tag{26}$$

where n is the number of the type of solution in (25) (i.e., when one of the N_i from group 1 is used, $n = 1$; when one of the N_i from group 2 is used, $n = 2$, etc.). It can be seen that the differences ($\ln Q_{\mathrm{c}}^{(n)} - \ln Q_{\mathrm{c}}^{(n')}$) depend only on n, n', N_0, x, and N_x. By calculating each of the $\ln Q_{\mathrm{c}}^{(n)}$ for values of x from 3 to 10 and values of v_0, the volume fraction of " solute molecules ", ($v_0 = N_0/(N_0 + xN_x)$) from 0.01 to 0.99 at intervals of 0.01, it can be shown that $\ln Q_{\mathrm{c}}^{(n)}$ for $n = 2$ through 5 is always less than either $\ln Q_{\mathrm{c}}^{(1)}$ or $\ln Q_{\mathrm{c}}^{(6)}$. In other words, systems represented by the four intermediate groups of solutions are always metastable with respect to a completely aligned system (1) or an isotropic system (6). At lower volume fractions of " solute molecules " an aligned arrangement is most stable, while an isotropic arrangement is most stable at higher volume fractions of " solute molecules ". Qualitatively, this behavior is the same as that exhibited by a lattice of non-interacting rods and holes; in fact, although the absolute values of the $\ln Q_{\mathrm{c}}^{(n)}$ are quite different in the two cases, the values of ($\ln Q_{\mathrm{c}}^{(n)} - \ln Q_{\mathrm{c}}^{(n')}$) are identical. Since the behavior of an athermal system of rods and holes will be discussed later, no more will be said concerning the special case where $w_{xx'} = w_{xx}$ except to note that W is the same for all the groups of solutions in (25).

As was noted earlier, when $w_{xx'} \neq w_{xx}$, equations (20) cannot in general be solved, which means that $\ln Q_{\mathrm{c}}(N_0, \mathbf{N}_i, \overline{N}_{0i}, \overline{N}_{i0}, \overline{N}_{ij})$ cannot be obtained and then maximized with respect to $\mathbf{N}_i$. However, given the discrete directional nature of the lattice, it seems reasonable to assume that could we perform the desired solution and subsequent maximization, the stable solutions for $\mathbf{N}_i$ would still be found among those in (25). Making this assumption, we can solve (20) for each of the six cases in (25) separately. The general result is

$$\overline{N}_{0i}^{(n)} = \overline{N}_{i0}^{(n)} = \frac{qzN_0N_i}{N_0 + qN_x + B^{(n)}} \qquad (i = 1, \ldots, n)$$

$$\overline{N}_{ij}^{(n)} = \overline{N}_{ji}^{(n)} = \frac{q^2zN_iN_j \exp[(2w - w')/(kT)]}{N_0 + [(2RF/n) - 1]qN_x + B^{(n)}} \qquad \left\{ \begin{array}{l} i = 1, \ldots, n \\ j = 1, \ldots, n \\ i \neq j \end{array} \right\} \tag{27}$$

where

$$F = (n - 1)\exp[-w'/(kT)] + 1$$
$$B^{(n)} = \sqrt{(N_0 - qN_x)^2 + (4RF/n)qN_0N_x} \qquad (28)$$

and n again refers to the numbered sets of solutions in (25). Finally, (27), (28), and (18) yield

$$\begin{aligned} \ln Q_c^{(n)} &= [nN - (x-1)N_x]\ln[N - (x-1)N_x/n] - N_0 \ln N_0 \\ &\quad - N_x \ln(N_x/n) - (n-1)N \ln N \\ &\quad - \frac{zN_0}{2}\ln\left\{\frac{2RF(N_0 + qN_x)}{n[\{(2RF/n) - 1\}N_0 + qN_x + B^{(n)}]}\right\} - \frac{qzN_x}{2} \\ &\quad \times \ln\left\{\frac{2R(N_0 + qN_x)}{N_0 + [(2RF/n) - 1]qN_x + B^{(n)}}\right\} - \frac{z}{2kT} \\ &\quad \times (N_0 w_{00} + qN_x w_{xx}) \end{aligned} \qquad (29)$$

Here the relative values of the $\ln Q_c{}^{(n)}$ are functions of w, w', and T as well as of n, n', x, and v_0. In order to find the stable solutions, the free energies of systems with $n = 1$ to 6 were calculated at $N = 100 \times 10^{23}$ for the following sets $\{x, w \times 10^{21}$ calories$\}$: $\{3, -2.5\}$, $\{5, -2.0\}$, $\{5, -1.5\}$, $\{7, -2.0\}$, $\{7, -1.5\}$, $\{10, -1.5\}$, and $\{10, -1.0\}$. At each x and w the calculations were performed for $w' = 1\%$, 2%, 5%, 7.5%, 10%, and 15% of $|w|$, and at each $\{x, w, w'\}$ for all possible combinations of v_0 and T within the ranges $v_0 = 0.30$ to 0.90 (intervals of 0.05) and $T = 300$ °K to 600 °K (intervals of 25 °K). In addition, volume fractions in the range 0.05 to 0.30 were used at $x = 3$ and $x = 5$. On the basis of the free energies obtained, it can be concluded that systems with N_i in groups 2 through 5 are again always metastable with respect to either an aligned (1) or an isotropic (6) arrangement. Since $(\ln Q_c{}^{\text{isotropic}} - \ln Q_c{}^{\text{aligned}})$ is now temperature dependent and $W^{\text{isotropic}}$ no longer equals W^{aligned}, a first-order aligned → isotropic phase transition, analogous to the nematic → isotropic transition in liquid crystals, is now observed. For the remainder of this paper, we shall restrict ourselves to considering this transition for a lattice of holes and interacting rods, since this special case is most relevant to an investigation of mesomorphic behavior. All our remarks concerning this system, however, can be directly extended to a lattice of " solute molecules " and rods. (Here, of course, two additional variables w_{00} and w_{0x} must be considered.) For rods and holes,

$$\begin{aligned} w_{00} &= w_{0x} = 0 \\ w &= -w_{xx}/2 \\ R &= \exp[-w_{xx}/(kT)]. \end{aligned} \tag{30}$$

Thus,

$$\begin{aligned} G_c^{\text{aligned}} = A_c^{\text{aligned}} = -\frac{zN_0}{2}w_{xx} + kT\Big\{&N_0 \ln N_0 + N_x \ln N_x \\ &- [N-(x-1)N_x]\ln[N-(x-1)N_x] \\ &+ \frac{zN_0}{2}\ln\left[\frac{2(N_0+qN_x)}{(2R-1)N_0+qN_x+\beta}\right] \\ &+ \frac{qzN_x}{2}\ln\left[\frac{2(N_0+qN_x)}{N_0+(2R-1)qN_x+\beta}\right]\Big\} \end{aligned} \tag{31}$$

$$\begin{aligned} G_c^{\text{isotropic}} = A_c^{\text{isotropic}} = \frac{-zN_0}{2}w_{xx} + kT\Big\{&N_0 \ln N_0 + N_x \ln(N_x/6) \\ &+ 5N\ln N - [6N-(x-1)N_x]\ln[N-(x-1)N_x/6] \\ &+ \frac{zN_0}{2}\ln\left[\frac{F(N_0+qN_x)}{3\{[(RF/3)-1]N_0+qN_x+\beta'\}}\right] \\ &+ \frac{qzN_x}{2}\ln\left[\frac{2(N_0+qN_x)}{N_0+[(RF/3)-1]qN_x+\beta'}\right]\Big\} \end{aligned} \tag{32}$$

$$F = 5\exp[-w'/(kT)] + 1, \tag{33}$$

$$\beta' = \sqrt{(N_0-qN_x)^2 + (2RF/3)qN_0N_x} \tag{34}$$

where G and A are the Gibbs and Helmholtz free energies, respectively. Furthermore,

$$E_c^{\text{aligned}} = H_c^{\text{aligned}} \qquad W^{\text{aligned}} = \frac{q^2zN_x^2w_{xx}R}{N_0+(2R-1)qN_x+\beta} \tag{35}$$

and
$$E_{\mathrm{c}}^{\mathrm{isotropic}} = H_{\mathrm{c}}^{\mathrm{isotropic}} = W^{\mathrm{isotropic}} = \frac{q^2 z N_x^2 R(F w_{xx} + 5w' \exp[-w'/(kT)])}{6[N_0 + [(RF/3) - 1]qN_x + \beta']} \tag{36}$$

where E and H denote internal energy and enthalpy, respectively. The remaining thermodynamic functions for both phases are readily obtained, but for our purposes the above are sufficient.

Results

In order to understand the present system properly, it is necessary to consider briefly the behavior of a system of *non-interacting* rods and holes on an fcc lattice, since $\ln g(N_0, \mathrm{N}_i)$ for the latter system enters directly into our expressions for $\ln Q_{\mathrm{c}}$. To this end, $-G/(kT)$ (or $\ln g\ (N_0, \mathrm{N}_i)$) for such a lattice is plotted in Fig. 1. The length-to-breadth ratio x of the rods is equal to 5 and N again equals 100×10^{23}. For v_0's below approximately 0.095, the aligned phase is more stable, while the isotropic phase is more stable for v_0's above this value. The same qualitative behavior is observed for all length-to-breadth ratios, but the value of v_0 at which the free energies of the two phases are equal varies strongly with x, as is shown in Fig. 2. For $x = 3$ and $x = 4$ this value of v_0 approaches zero, but this is not the case for $x \geqslant 5$.‡ At $x = 10$, v_0 has reached approximately 0.56. Such behavior is physically reasonable qualitatively, since the longer the rods become, the more space is needed to accommodate them in an isotropic arrangement. As a result of the incompressibility of the lattice, the small number of allowed directions, and the complete inflexibility of the rods, however, the effect is greatly exaggerated here. Since it stems from the basic nature of our model, this defect cannot be eliminated, which means that for $x \geqslant 5$ we are forced to investigate systems with larger free volumes than those normally observed for pure substances and that the v_0's which must be used increase with increasing x. Since our model was not meant to be a replica of any real system, but

‡ It has recently been determined that the isotropic phase is stable at all volume fractions of holes V_0 for $X < 4.55$ (approximately)—NOTE ADDED IN PROOF.

merely to incorporate a few fundamental properties of nematogenic substances, this is inconvenient but not a serious obstacle to fulfilling our purpose.

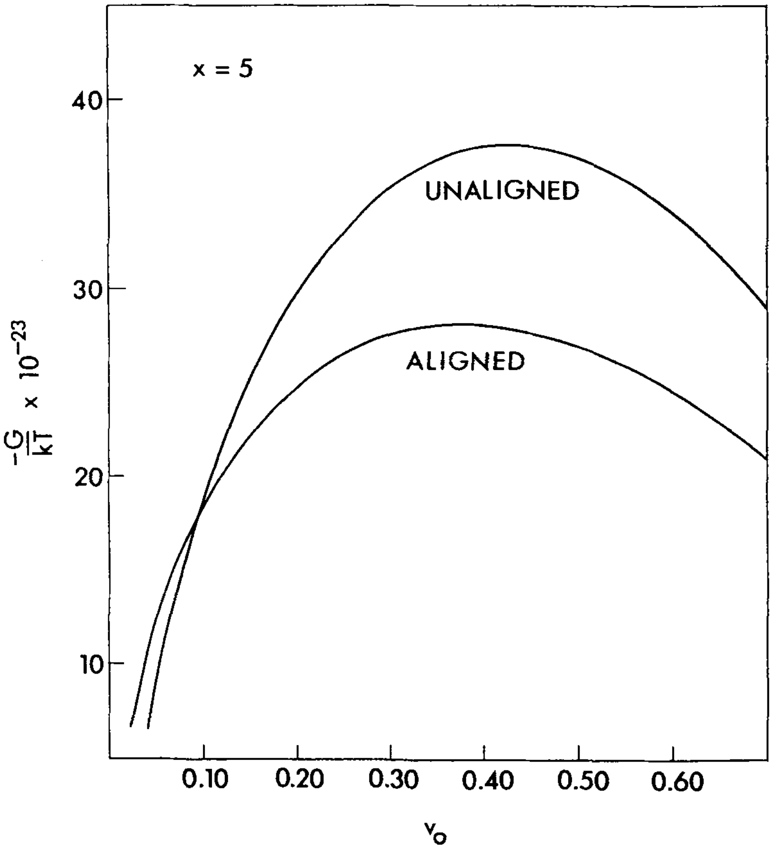

Figure 1. Dependence of the free energy on the volume fraction of holes v_0 for an athermal lattice of rods and holes.

The behavior of our aligned-isotropic transition can now be considered. Specifically, the dependencies of the transition temperature T_{trans} and the enthalpy of transition ΔH_{trans} on the variables w_{xx}, $(w_{xx'} - w_{xx})$, v_0, and x will be illustrated by means of the remaining seven figures. The transition temperatures have been determined to the nearest degree and the enthalpies to the

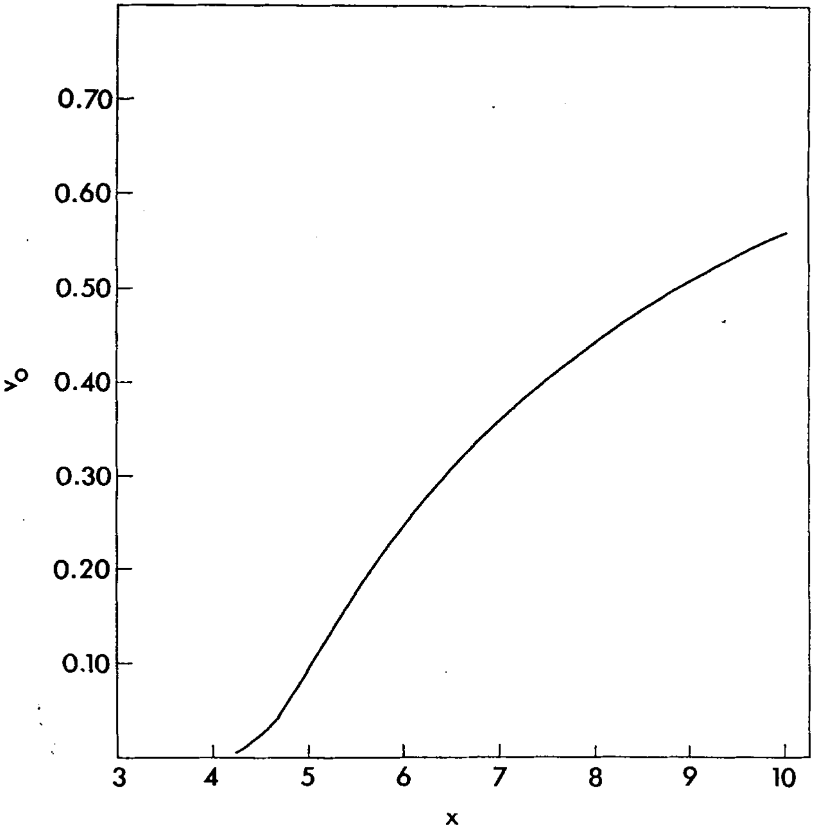

Figure 2. Dependence of the transition volume fraction of holes v_0 on the length-to-breadth ratio x of the rods for an athermal lattice.

nearest calorie/mole. All computations were performed on an IBM 360 Model 40 computer using two Fortran IV(G) programs, the first of which locates transitions to within 25 °K and the second of which calculates G_c and H_c for both phases at 1° intervals over this 25° range. Approximately 100 sets of variables $\{x, w_{xx}, (w_{xx'} - w_{xx}), v_0\}$ in addition to the over 600 such sets mentioned previously were run through the first program, while the transition temperatures (± .5°) and enthalpies were determined for 165 different combinations of variables.

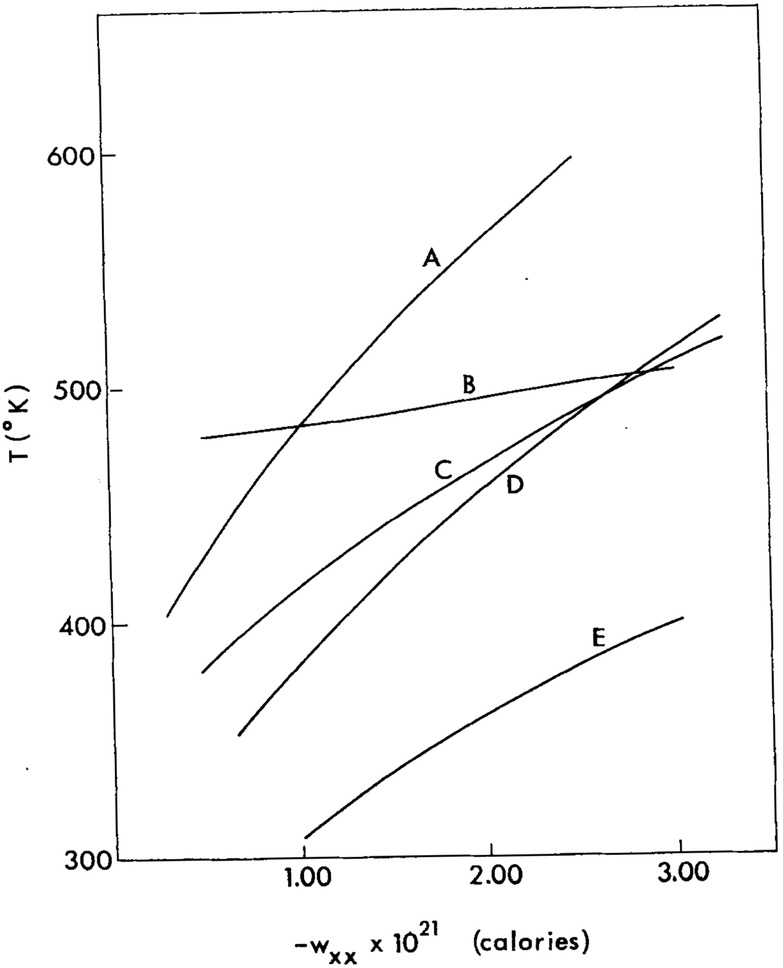

Figure 3. Dependence of the transition temperature T on the segment interaction energy w_{xx}.

(A) $x = 10$, $v_0 = 0.65$, $(w_{xx'} - w_{xx}) = 4.0 \times 10^{-23}$ cal.;
(B) $x = 5$, $v_0 = 0.15$, $(w_{xx'} - w_{xx}) = 1.5 \times 10^{-23}$ cal.;
(C) $x = 7$, $v_0 = 0.50$, $(w_{xx'} - w_{xx}) = 4.0 \times 10^{-23}$ cal.;
(D) $x = 10$, $v_0 = 0.65$, $(w_{xx'} - w_{xx}) = 3.0 \times 10^{-23}$ cal.;
(E) $x = 7$, $v_0 = 0.55$, $(w_{xx'} - w_{xx}) = 4.0 \times 10^{-23}$ cal.

Figure 3 shows the dependence of transition temperature on the segment interaction energy w_{xx}. As is apparent, T_{trans} is rather sensitive to w_{xx} at larger values of x and of $(w_{xx'} - w_{xx})$, but less so for smaller x and $(w_{xx'} - w_{xx})$. The increase in T_{trans} with increasing strength of the average interactions is in agreement with the experimental behavior of real systems; i.e., the nematic-isotropic transition temperature is found to rise when more strongly interacting groups, either more polar or more polarizable, are introduced into a nematogenic molecule, provided that the addition does not appreciably broaden the molecule.

Figure 4 illustrates the dependence of the enthalpy of transition on w_{xx}. ΔH_{trans} is more sensitive to w_{xx} than is T_{trans} because both the enthalpy and entropy of transition increase as $|w_{xx}|$ increases, with the proportionately greater increase occurring in the enthalpy. It should be noted that the range of w_{xx} used for Figs. 3 and 4 was chosen by estimating the molar heats of vaporization ΔH_v for various nematogenic substances and then obtaining w_{xx}'s from the approximate relationship

$$\Delta H_v \approx \frac{qzN_x}{2} w_{xx} \tag{37}$$

In Figures 5 and 6, T_{trans} and ΔH_{trans}, respectively, are plotted against $(w_{xx'} - w_{xx})$ for a variety of systems. In Fig. 5 the plots are linear while in Fig. 6 they deviate from linearity, particularly at larger values of $(w_{xx'} - w_{xx})$ – behavior that is difficult to interpret since an explicit expression for T_{trans} cannot be derived. The enhanced sensitivity of T_{trans} to changes in $(w_{xx'} - w_{xx})$, relative to that of ΔH_{trans} results from a decrease in ΔS_{trans} as the alignment of the rods increases with increasing $(w_{xx'} - w_{xx})$. The " bunching " of the curves in Fig. 6 occurs primarily because ΔH_{trans} is much less dependent upon v_0 than is T_{trans}. In both figures, the range of $(w_{xx'} - w_{xx})$ used represents values of $w_{xx'}$ from approximately $96\frac{1}{2}\%$ to approximately $99\frac{2}{3}\%$ of w_{xx}. Although a transition can be made to occur in any given temperature range through a skillful balancing of $(w_{xx'} - w_{xx})$ and

v_0, it is important to note that when this balancing is performed to give transition temperatures in the range normally observed for nematic-isotropic transitions, the resulting systems always have enthalpies of transition within the experimentally observed range of values. Finally, while the strong dependencies of both T_{trans} and ΔH_{trans} on $(w_{xx'} - w_{xx})$ are intuitively reasonable, they are difficult to compare with the behavior of real mesophases because the physical meaning of the quantity $(w_{xx'} - w_{xx})$ is not clear. Nematic alignment must be favored energetically in some manner in order for the nematic-isotropic transition to be first order, but the origin of this energy advantage is uncertain. Gray[6] suggests that it arises in large part from residual terminal attractions between molecules. Another possibility is simply that rod-like molecules can approach each other more closely and interact more effectively in a nematic phase than in an isotropic phase. Both these factors, as well as more subtle and complex forces, may be operative in real systems.

Figure 7 illustrates the very strong dependence of transition temperature on volume fraction of holes (or density) for our model. T_{trans} decreases so sharply with increasing v_0 because an increase in v_0 causes a much more marked enhancement in ΔS_{trans} than in ΔH_{trans}, the primary effect of adding holes to the lattice being an increase in the number of possible configurations for an isotropic arrangement of the rods relative to the number of possible configurations for an aligned arrangement.

Figure 8 shows that ΔH_{trans} rises with increasing v_0, although this rise is much less marked than the corresponding decrease in T_{trans}. Mathematically, the reason for the increase is that $\sum_i \bar{N}_{ii}$ decreases more (proportionately) for the isotropic phase than for the aligned phase as the result of an increase in v_0. Physically, this probably means that the more free space there is in the system, the more truly isotropic the arrangement of the rods can become within small regions of the lattice, resulting in fewer neighboring aligned rods. Too few density measurements on nematogenic substances are available in the literature to discern any trends with which to compare this behavior or that shown in Fig. 7.

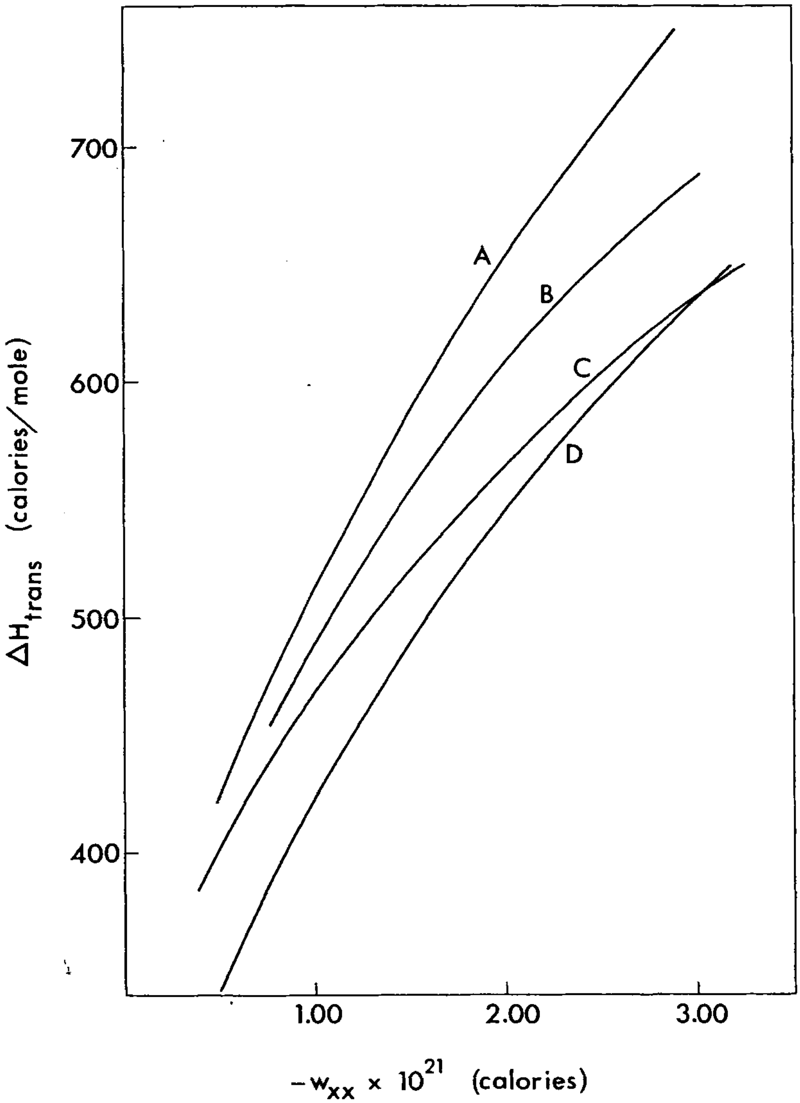

Figure 4. Dependence of the enthalpy of transition ΔH_{trans} on the segment interaction energy w_{xx}.

(A) $x = 10, v_0 = 0.65, (w_{xx'} - w_{xx}) = 4.0 \times 10^{-23}$ cal.;
(B) $x = 7, v_0 = 0.55, (w_{xx'} - w_{xx}) = 4.0 \times 10^{-23}$ cal.;
(C) $x = 7, v_0 = 0.50, (w_{xx'} - w_{xx}) = 4.0 \times 10^{-23}$ cal.;
(D) $x = 10, v_0 = 0.65, (w_{xx'} - w_{xx}) = 3.0 \times 10^{-23}$ cal.

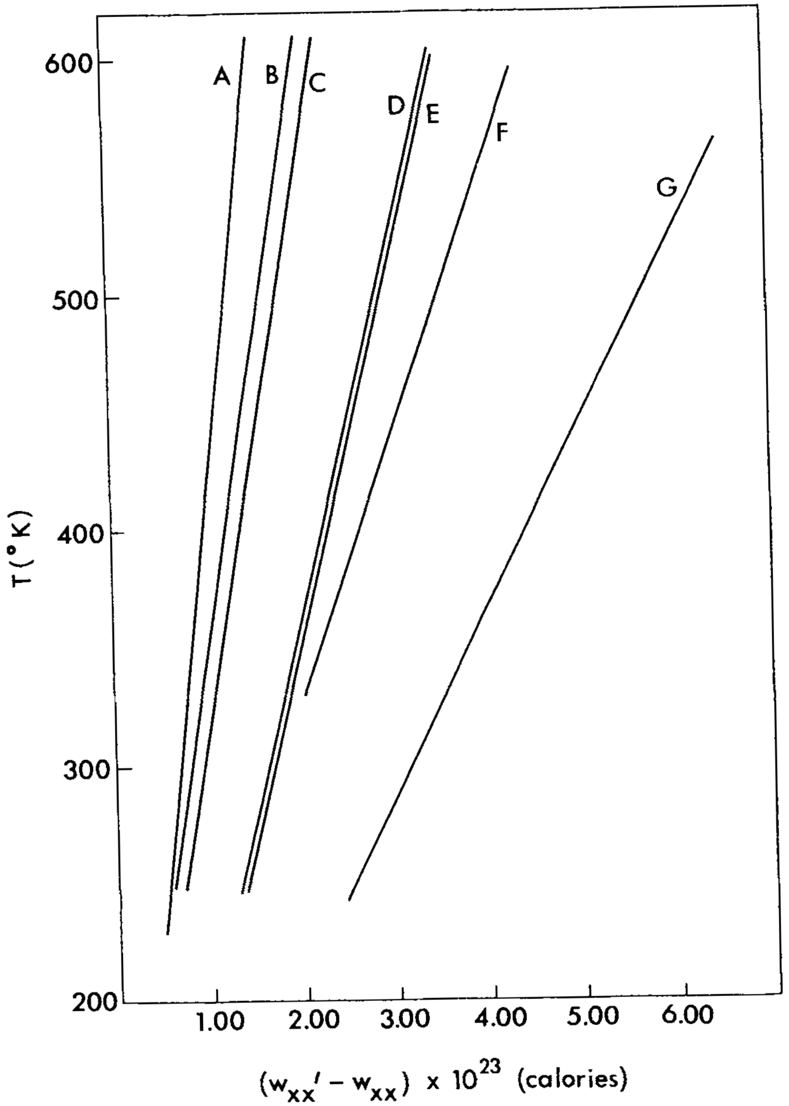

Figure 5. Dependence of the transition temperature T on the difference in segment interaction energies $(w_{xx'} - w_{xx})$.

(A) $x = 7$, $v_0 = 0.40$, $w_{xx} = -1.5 \times 10^{-21}$ cal.;
(B) $x = 10$, $v_0 = 0.60$, $w_{xx} = -1.5 \times 10^{-21}$ cal.;
(C) $x = 10$, $v_0 = 0.60$, $w_{xx} = -1.0 \times 10^{-21}$ cal.;
(D) $x = 5$, $v_0 = 0.20$, $w_{xx} = -2.0 \times 10^{-21}$ cal.;
(E) $x = 5$, $v_0 = 0.20$, $w_{xx} = -1.5 \times 10^{-21}$ cal.;
(F) $x = 9$, $v_0 = 0.60$, $w_{xx} = -1.5 \times 10^{-21}$ cal.;
(G) $x = 5$, $v_0 = 0.30$, $w_{xx} = -2.0 \times 10^{-21}$ cal.

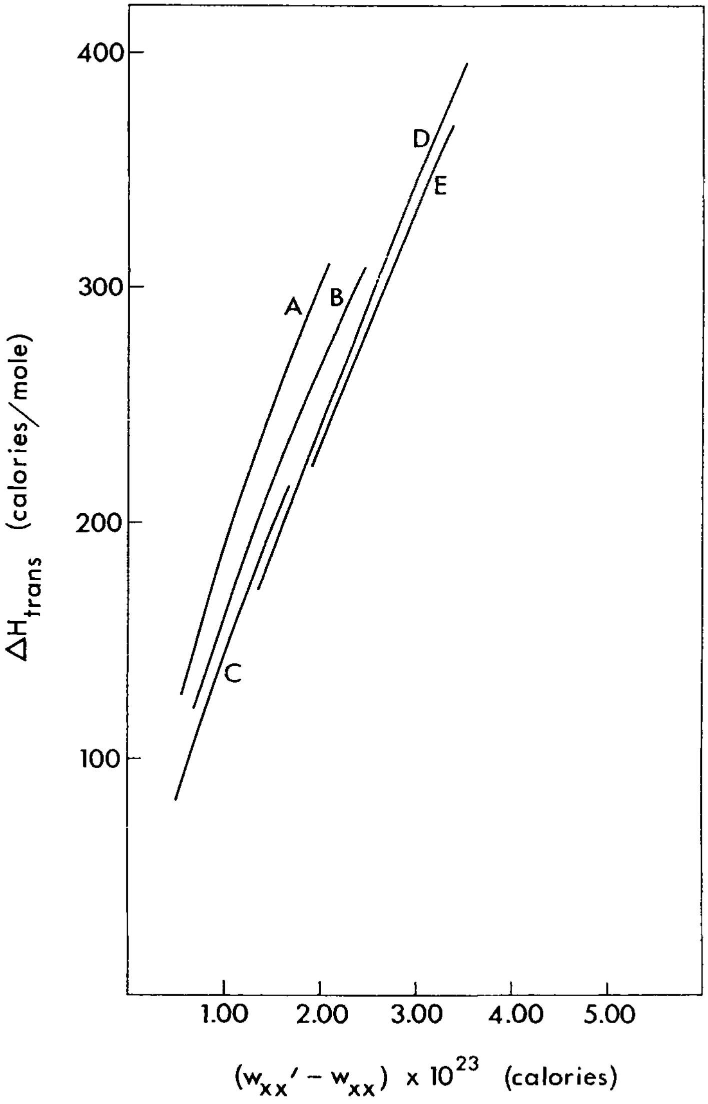

Figure 6. Dependence of the enthalpy of transition $\Delta H_{\mathrm{trans}}$ on the difference in segment interaction energies $(w_{xx'} - w_{xx})$.

(A) $x = 10$, $v_0 = 0.60$, $w_{xx} = -1.5 \times 10^{-21}$ cal.;
(B) $x = 10$, $v_0 = 0.60$, $w_{xx} = -1.0 \times 10^{-21}$ cal.;
(C) $x = 7$, $v_0 = 0.40$, $w_{xx} = -1.5 \times 10^{-21}$ cal.;
(D) $x = 5$, $v_0 = 0.20$, $w_{xx} = -2.0 \times 10^{-21}$ cal.;
(E) $x = 5$, $v_0 = 0.20$, $w_{xx} = -1.5 \times 10^{-21}$ cal.

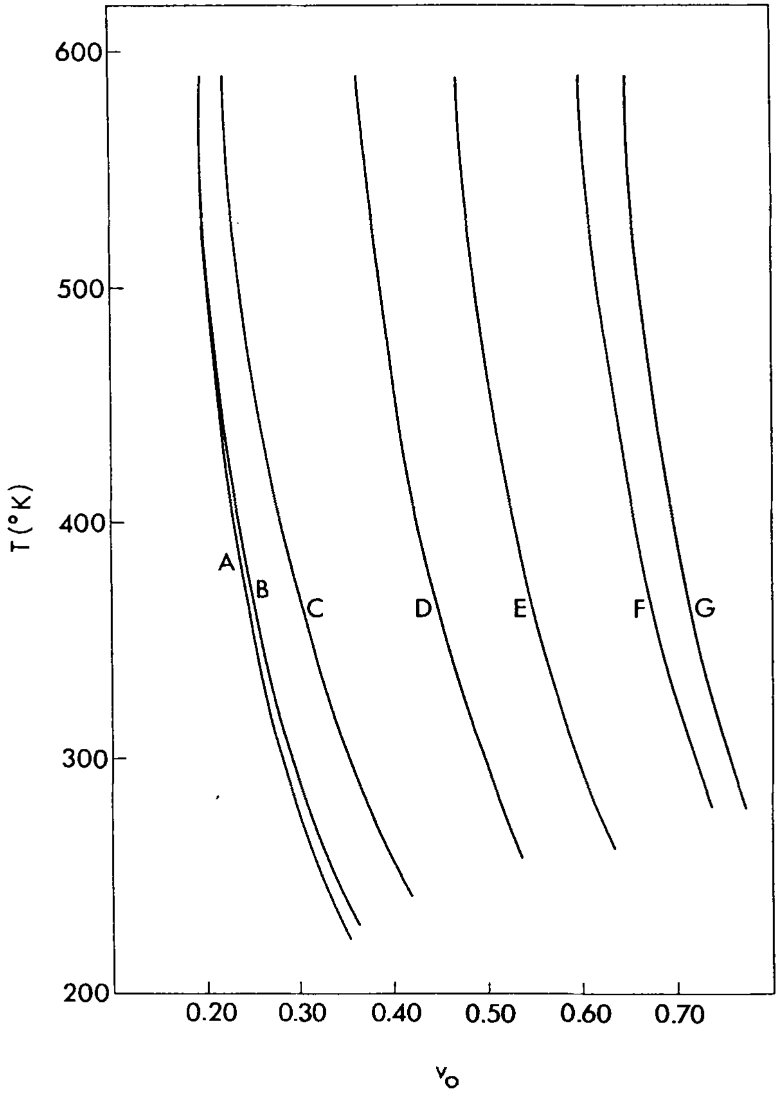

Figure 7. Dependence of the transition temperature T on the volume fraction of holes v_0.

(A) $x = 5$, $w_{xx} = -1.5 \times 10^{-21}$ cal., $(w_{xx'} - w_{xx}) = 3.0 \times 10^{-23}$ cal.;
(B) $x = 5$, $w_{xx} = -2.0 \times 10^{-21}$ cal., $(w_{xx'} - w_{xx}) = 3.0 \times 10^{-23}$ cal.;
(C) $x = 5$;
(D) $x = 6$;
(E) $x = 7$;
(F) $x = 9$;
(G) $x = 10$.

In curves (C) through (G),
$w_{xx} = -2.0 \times 10^{-21}$ cal. and $(w_{xx'} - w_{xx}) = 4.0 \times 10^{-23}$ cal.

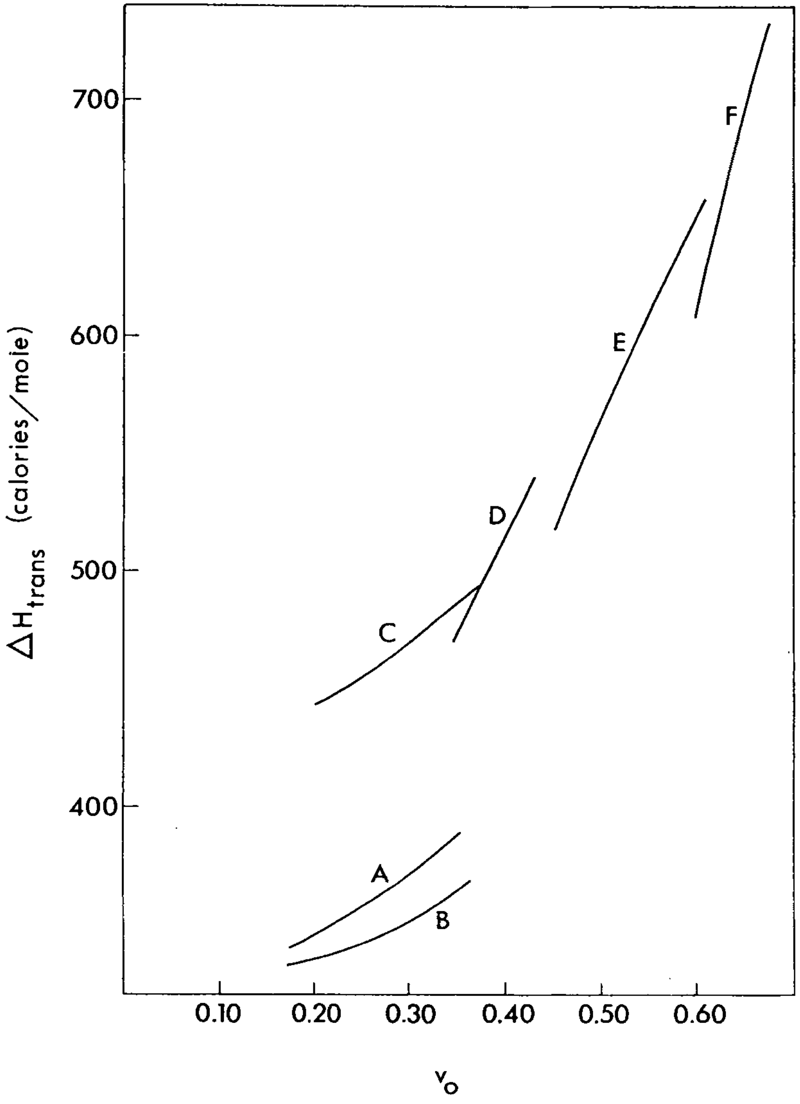

Figure 8. Dependence of the enthalpy of transition ΔH_{trans} on the volume fraction of holes v_0.

(A) $x = 5, w_{xx} = -2.0 \times 10^{-21}$ cal., $(w_{xx'} - w_{xx}) = 3.0 \times 10^{-23}$ cal.;
(B) $x = 5, w_{xx} = -1.5 \times 10^{-21}$ cal., $(w_{xx'} - w_{xx}) = 3.0 \times 10^{-23}$ cal.;
(C) $x = 5$;
(D) $x = 6$;
(E) $x = 7$;
(F) $x = 9$.

In curves (C) through (F),
$w_{xx} = -2.0 \times 10^{-21}$ cal. and $(w_{xx'} - w_{xx}) = 4.0 \times 10^{-23}$ cal.

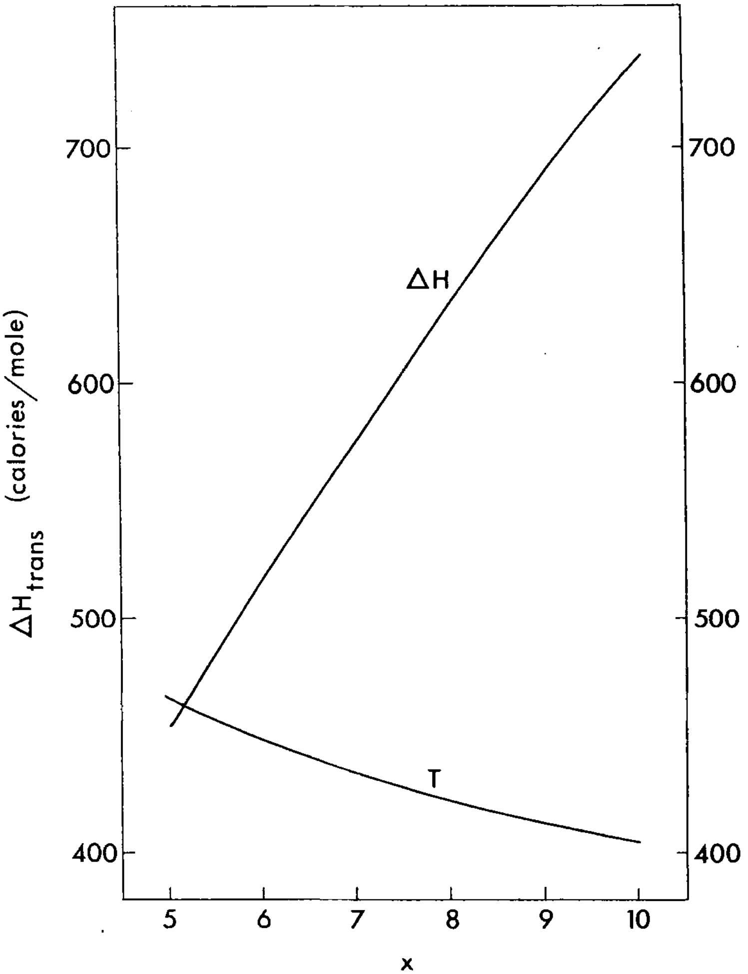

Figure 9. Dependence of the transition temperature T and of the enthalpy of transition ΔH_{trans} on the length-to-breadth ratio x of the rods.

The dependence of T_{trans} and of ΔH_{trans} on x cannot be ascertained directly for our model since it is necessary to work in a different range of v_0 at each value of x in order to obtain meaningful results, as demonstrated by Fig. 7. Rather, these dependencies must be determined indirectly. Increasing x, holding w_{xx} and

$(w_{xx'} - w_{xx})$ constant, will clearly have two effects on our system: first, the actual lengthening of the rods should result in increases in both T_{trans} and ΔH_{trans}; second, as the rods get longer, the free volume of the system will increase, causing T_{trans} to decrease sharply and ΔH_{trans} to rise less sharply. These two effects reinforce one another with respect to ΔH_{trans} but are in opposition with respect to T_{trans}. Let us assume that the second effect will be dominant in the case of the transition temperatures—a reasonable assumption, given the extremely strong dependence of T_{trans} on v_0, and one which leads to the experimentally observed trend. Then, as the length of the rods increases, T_{trans} will decrease while ΔH_{trans} will increase. Although the absolute magnitudes of these changes cannot be determined, since we do not know quantitatively how v_0 depends on x, their relative magnitudes can be ascertained by devising an x-dependence for v_0 so as to obtain a reasonable downward trend in T_{trans}, and then observing the resulting dependence of ΔH_{trans} on x. Figure 9 gives the result of this procedure for a system with $w_{xx} = -2.0 \times 10^{-21}$ calories and $(w_{xx'} - w_{xx}) = 4.0 \times 10^{-23}$ calories. A value of v_0 was chosen at each x in order to produce a gradual decrease in T_{trans} with increasing x of the order of magnitude of those actually observed in ascending various homologous series of nematogenic compounds. The sets (x, v_0) used for this purpose were (5, 0.25), (6, 0.40), (7, 0.51), (9, 0.66), and (10, 0.69). The same sets were then used to determine the dependence of ΔH_{trans} on x. As can be seen, the rise in ΔH_{trans} obtained is much steeper than the corresponding decline in T_{trans}, in agreement with experiment. For example, for the even carbon-numbered members of the homologous series of the p,p'-dialkoxyazoxybenzenes from p-azoxyphenetole to the decyl homologue, the transition temperatures decrease smoothly with increasing alkyl chain length from 167.5 °C for the former to 123.4 °C for the latter, while the enthalpies of transition, as measured by Arnold,[7] increase from 1500 joules/mole to 4930 joules/mole. (It should be noted that for such a homologous series, increasing the alkyl chain length by two methyl groups increases the length-to-breadth ratio by one, approximately).

Conclusions

Our model incorporates four major characteristics of nematogenic substances: (1) the rod-like nature of the particles, (2) the possibility of varying degrees of order in the system, (3) attractive forces acting between particles, (4) possible energetic favoring of anisotropy in the system. It does not incorporate a number of other important features of real substances, such as the temperature dependence of the density and the occurrence of PV changes. Within these limits, the model can predict the gross qualitative behavior of nematogenic systems at their nematic-isotropic transitions, to the extent, at least, that this behavior is known and understood. Most significant in this regard is its ability to explain the concurrent decreases in transition temperatures and increases in enthalpies of transition which occur in ascending a homologous series of nematogenic compounds and to predict that the latter changes are of considerably greater magnitude than the former. For our system, this behavior is caused, as was explained earlier, by the superposition of two effects: an increase in T_{trans} and in ΔH_{trans} caused by the actual lengthening of the rods, and a decrease in T_{trans} and an increase in ΔH_{trans} caused by an increase in v_0 with increasing x. In a real system this should still be the case since both these effects should still be present. Furthermore, $\Delta v_{0\text{trans}}$ as well as the values of v_0 for both phases would be expected to increase with increasing x, since the longer the molecules become, the more free volume should be required to accommodate them in an isotropic distribution relative to that required for a nematic distribution. This increase in $\Delta v_{0\,trans}$ should produce a corresponding decrease in the strength of the intermolecular attractions in the isotropic phase relative to their strength in the nematic phase, causing the nematic phase to become more energetically favored as the homologous series is ascended. In terms of our model system, this is equivalent to our increasing $(w_{xx'} - w_{xx})$ as x increases, which, were it done, would lessen the predicted decline in T_{trans} with increasing x and enhance the corresponding rise in ΔH_{trans}, making the model correspond still more closely with reality.

Thus, it appears that the configurational partition function of our simple model is sufficient to provide quite reasonable explanations for (1) the occurrence of the nematic-isotropic transition (i.e., this transition occurs when the configurational entropy to be gained from an isotropic distribution of the molecular long axes is sufficient to counterbalance the energy advantage of a nematic distribution arising from the intermolecular attractive forces of the system), (2) the observed increases in T_{trans} with increases in the strength of the intermolecular attractions, (3) the magnitude of experimental values of ΔH_{trans}, and (4) the observed trends in T_{trans} and ΔH_{trans} along homologous series of nematogenic compounds. The reasonableness of these explanations is no assurance of their correctness, of course, and other possible explanations can be put forth. For example, it may be possible to explain the trends in T_{trans} and ΔH_{trans} along homologous series on the basis of the vibrational partition functions of the systems in question; that is, if internal rotations about C—C bonds are considerably less hindered in isotropic phases than in nematic phases, there should be significant vibrational contributions to ΔH_{trans} and ΔS_{trans} which should, of course, increase with increasing alkyl chain length. If, furthermore, the entropy contribution were to increase more sharply than the enthalpy contribution with increasing chain length, the result would be a decrease in T_{trans} accompanying the increase in ΔH_{trans}. Although available experimental data[8] comparing the infrared spectra of nematic mesophases and their isotropic liquids point to no significant vibrational effects at the transition, more IR as well as Raman data on a variety of nematogenic substances are needed before a " vibrational explanation " of the observed trends in ΔH_{trans} and T_{trans} can be eliminated from consideration.

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