

many of the literally hundreds of other well-characterized solution lumirearrangements will also be found to have totally different solid-state counterparts? Perusal of the photochemical literature reveals a number of systems which may be expected to exhibit case I or case II behavior. In addition, there are several examples of systems which likely react via nonminimum energy conformations in solution and which might therefore show different photobehavior in the solid state via case III mechanisms.

Not only is the synthetic potential of organic photochemistry enhanced by findings such as those reported in this Account, but with the use of X-ray crystallography, deeper insights into the mechanistic structure-

reactivity relationships involved in organic photorearrangements are possible. In short, studies of organic solid-state unimolecular photoprocesses are likely to provide fascinating and useful results for some time to come.

I wish to express my deepest gratitude to the individuals who carried out the work described. Dr. Alice Dzakpasu, Dr. Wolfgang Appel, and Leueen Walsh were involved in the organic photochemistry, and Dr. Simon Phillips and Dr. Trevor Greenhough performed the X-ray crystallography. It is a special pleasure to acknowledge the invaluable contributions of my colleague, Dr. James Trotter, to the project. Finally, I am grateful to the Natural Sciences and Engineering Research Council of Canada and the Petroleum Research Fund for financial support.

A van der Waals Picture of the Isotropic-Nematic Liquid Crystal Phase Transition

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Long-range orientationally ordered states of liquids composed of elongated, flat molecules have been known for almost a century.¹ The simplest fluid-fluid transition involving these "liquid crystal" systems takes place between the normal isotropic phase and a nematic state where the long molecular axes tend to lie along a preferred direction. But in the nematic state there is *no* long-range ordering of the centers of mass. Thus the system retains to a great extent many of the familiar properties, e.g., viscosity, characteristic of ordinary liquids. Only in the solid phase do we find long-range ordering of both the molecular orientations and centers of mass: hence the name "liquid crystal" for the nematic state.

In a liquid crystal, each molecule interacts with its neighbors via forces which depend on their mutual orientations. To "keep out of each other's way", i.e., to minimize repulsions, a parallel configuration is optimal; in addition this arrangement enhances the pair attractions. Recall that the thermodynamic free energy, A , is a balance between the total interaction energy, E , and the temperature-weighted entropy, TS ; $A = E - TS$. Thus, at low enough temperature we expect that the lowering of E which comes about from parallel arrangements of molecules will become sufficient to offset

the decrease in S attendant upon this long-range alignment. The likelihood of this happening before the freezing (liquid \rightarrow solid) temperature is reached depends of course on the intermolecular potential being properly anisotropic. The ultimate goal of any theory of liquid crystals must then be to account for why the phase diagrams for thousands of compounds include an "extra", orientationally ordered fluid, region whereas those for hundreds of thousands of others show only the usual fluid and solid phases.²

The transition between isotropic and nematic states is observed to be first order, but the differences in density (ρ), enthalpy (H), and entropy (S) between the coexisting phases are dramatically small. Consider, for example, the prototype liquid crystal forming molecule *p*-azoxyanisole (PAA) shown in Figure 1. When it is cooled below 408 K at atmospheric pressure, it undergoes a first-order transformation from the isotropic to nematic phase: the associated discontinuities are as small as $\Delta\rho/\bar{\rho} \approx 0.0035$, $\Delta H \approx 0.14$ kcal/mol, and $\Delta S \approx 0.34$ cal/(mol K).³ (Here $\bar{\rho}$ is the average of the densities of the coexisting phases.) Upon further cooling of the nematic state it is transformed near $T = 390$ K to a solid; at the freezing transition the discontinuities are larger by one to two orders of magnitude—the values of $\Delta\rho/\bar{\rho}$, ΔH , and ΔS are 0.11, 7.1 kcal/mol, and 18 cal/(mol K).⁴

Descriptions of the isotropic-nematic transition have been largely phenomenological,⁵ but recently there have

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(1) For mention of early work on liquid crystals, see the references given in the review by G. W. Gray, *Adv. Liquid Cryst.* 2, 1 (1976).

(2) See, for example, the tabulations provided by D. Demus, H. Demus, and H. Zschke, *Flüssige-Kristallen in Tabellen* (1974).

(3) W. Maier and A. Saupe, *Z. Naturforsch., A*, 14A, 882 (1959); 15A, 287 (1960), for $\Delta\rho/\bar{\rho}$; H. Arnold, *Z. Phys. Chem. (Leipzig)*, 226, 146 (1964), for ΔH and ΔS .

(4) B. Deloche, B. Cabane, and D. Jerome, *Mol. Cryst.*, 15, 1975 (1971).

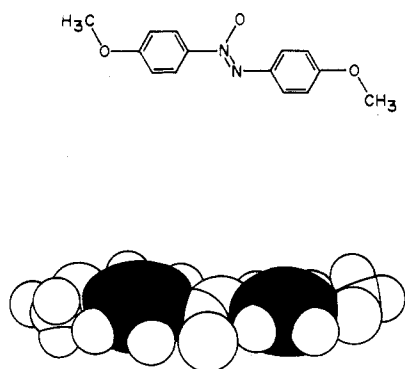


Figure 1. Schematic rendering of the *p*-azoxyanisole (PAA) molecule.

been attempts to provide a molecular-level statistical-mechanical theory. These latter attempts can be roughly divided into three categories according to whether the orientational ordering is assumed to be driven primarily by the angle-dependent attractions between molecules, by the anisotropic repulsive forces, or by both. Dominant in the first category are the Maier-Saupe-Luckhurst-Chandrasekhar mean-field theories in which all of the relevant thermodynamics is associated with an effective (mean) angle-dependent potential which acts separately on each molecule.⁶ Basic to the second approach is the hard-rod reference system which has been treated alternately via lattice models⁷ and classical liquid theories.⁸ The effects of anisotropy in both the intermolecular attractions and repulsions have been treated by Kimura⁹ for low-density fluids and by Ypma and Vertogen¹⁰ via perturbation expansions about an isotropic reference system. Shih, Lin-Liu, and Woo¹¹ have also included both repulsions and attractions, handling the spatial correlations by means of a conventional liquid theory and subjecting the orientational ordering alone to a mean-field approximation.

For the general case of arbitrary fluid density and molecular anisotropy, it has proved most useful to employ the van der Waals approach¹²⁻¹⁴ which is the subject of this Account; here the hard-anisotropic-core repulsions are treated as accurately as possible whereas

the longer ranged, weaker attractions are mean field averaged.

The van der Waals Picture

Over a hundred years ago, van der Waals suggested¹⁵ that the structure and thermodynamic properties of simple fluids could be interpreted in terms of nearly separate contributions from intermolecular repulsions and attractions. He asserted in particular that the repulsive forces were the same as for "hard spheres" and that the attractive potential of "mean field" felt by a molecule was essentially uniform, since it involved a sum over many long-range and slowly varying pair interactions. The depth of this negative background is proportional to the number of molecules contributing to it, and hence to the number density $\rho \equiv N/V$; thus the potential energy per molecule is

$$\frac{E}{N} = \frac{1}{2}a\rho \quad (a < 0) \quad (1)$$

We have chosen " $1/2 a$ " for the proportionality constant here to be consistent with the notation in our earlier work.¹²

Because the background attraction has no gradient, it leads to no forces on the hard spheres which are "immersed" in it, and the equilibrium configuration of the latter is the same as if only the repulsions were present.¹⁶ Then it follows that

$$S = S_{hs} \quad (2)$$

where S is the configurational entropy of the hard sphere (hs) system in the presence of the uniform attraction. From (1) and (2), and $A_{hs} = -TS_{hs} = -TS(E_{hs} = 0)$, we have

$$P \equiv -\left(\frac{\partial A}{\partial V}\right)_T \equiv \left[\frac{\partial}{\partial V}(TS - E)\right]_T = P_{hs} + \frac{1}{2}a\rho^2 = P_{GVDW} \quad (3)$$

If we replace the hard-sphere pressure P_{hs} by the appropriate (exact) form for a one-dimensional system, i.e., $P_{hs} = \rho kT/(1 - b\rho)$ where b is half the pair excluded volume, then (3) becomes the familiar van der Waals (VDW) equation. When, however, P_{hs} is allowed to represent the actual pressure of a three-dimensional hard-sphere fluid, then the resulting generalized van der Waals (GVDW) equation of state is expected to work well in describing the properties of simple dense fluids away from their critical points.

For example, when P_{hs} is taken from the computer studies of Alder and Wainwright,¹⁷ calculations of several dimensionless thermodynamic properties, e.g., the ratio of liquid to solid volume or the molecular entropy of fusion in units of Boltzmann's constant, have been shown^{16b} to agree very closely with experimental data on argon near its triple point. Furthermore, eq 3 has been derived from "first principles" by Kac, Uhlenbeck, and Hemmer,¹⁸ who studied the statistical mechanics of systems interacting via pair potentials which can be

(15) J. D. van der Waals, Dissertation, Leiden, 1873; English translation, Threlfall and Adair, *Phys. Memoirs*, 1, 333 (1890).

(16) Here we follow the exposition of van der Waals theory given by (a) B. Widom, *Science*, 157, 375 (1967); (b) H. C. Longuet-Higgins and B. Widom, *Mol. Phys.*, 8, 549 (1964).

(17) B. J. Alder and T. E. Wainwright, *J. Chem. Phys.*, 33, 1439 (1960).

(18) G. Stell, J. L. Lebowitz, S. Gaer, and W. Theumann (*J. Math. Phys.*, 7, 1532 (1966)) and M. Kac, G. E. Uhlenbeck, and P. C. Hemmer (*ibid.*, 4, 216 (1963)) are among the latest and earliest of the original series of papers on GVDW theory.

(5) See the monographs by P. G. de Gennes ("The Physics of Liquid Crystals", Oxford University Press, Oxford, 1974), E. B. Priestley, P. J. Wojtowicz, and P. Sheng ("Introduction to Liquid Crystals", Plenum Press, New York, 1974), and S. Chandrasekhar ("Liquid Crystals", Cambridge University Press, London, 1977) for comprehensive discussion of the Landau (de Gennes) and continuum (hydrodynamic-viscoelastic) theories of liquid crystals. These theories are also discussed extensively in M. J. Stephen and J. P. Straley, *Rev. Mod. Phys.*, 46, 617 (1974).

(6) These developments are reviewed, with appropriate lists of references, in the already cited⁵ monographs by Priestley et al. (Chapter 2) and Chandrasekhar (Chapter 2).

(7) F. Dowell and D. E. Martire, *J. Chem. Phys.*, 68, 1088, 1094 (1978), and references cited therein.

(8) M. A. Cotter, in "Proceedings of the NATO Advanced Study Institute on The Molecular Physics of Liquid Crystals", G. W. Gray and G. R. Luckhurst, Eds., Plenum Press, New York, 1978; see also J. D. Parsons, *Phys. Rev. A*, 19, 1225 (1979); R. Pynn, *J. Chem. Phys.*, 60, 4579 (1974); *Solid State Commun.*, 14, 29 (1974).

(9) H. Kimura, *J. Phys. Soc. Jpn.*, 36, 1280 (1974).

(10) J. G. T. Ypma and G. Vertogen, *Phys. Rev. A*, 17, 1490 (1978).

(11) Y. M. Shih, Y. R. Lin-Liu, and C.-W. Woo, *Phys. Rev. A*, 14, 1895 (1976).

(12) (a) W. M. Gelbart and B. A. Baron, *J. Chem. Phys.*, 66, 207 (1977); (b) W. M. Gelbart and A. Gelbart, *Mol. Phys.*, 33, 1387 (1977); (c) B. A. Baron and W. M. Gelbart, *J. Chem. Phys.*, 67, 5745 (1977).

(13) (a) M. A. Cotter, *J. Chem. Phys.*, 66, 1098 (1977); (b) *ibid.*, 67, 4268 (1977), and "The Van der Waals Approach to Nematic Liquids", in ref 8.

(14) A. Wulf, *J. Chem. Phys.*, 67, 2254 (1977).

decomposed into a hard-core repulsion plus an attraction having magnitude $\sim\gamma$ and range $\sim 1/\gamma$. They showed that eq 3 is exact in the limit $\gamma \rightarrow 0$.

Recall that eq 3 is equivalent to the Helmholtz free energy having the form

$$A_{\text{GVDW}} = A_{\text{hs}} + \frac{1}{2}N\psi \quad (4)$$

where

$$\psi = \rho a \quad (5)$$

is the mean attraction felt by a single molecule ($E = \frac{1}{2}N\psi$), and a is the average value of the pair attraction—according to van der Waals¹⁵ it is given by

$$a = \int' d\mathbf{r} u_{\text{attr}}(r) \quad (a < 0) \quad (6)$$

The prime on the integral in (6) assures that the average is taken only over those separations \mathbf{r} which do not violate the pair-excluded volume conditions; i.e., for hard spheres of diameter σ we have $|\mathbf{r}| \geq \sigma$.

Gelbart and Baron^{12a} showed that eq 4–6 could be generalized. Their original derivation has been superseded by a more recent formulation¹⁹ in which the atomic fluid approach¹⁸ is followed more closely. In particular, when the GVDW theory is applied to molecular fluids whose pair interactions are orientation dependent and which in addition can exist in liquid crystal phases, we find

$$A_{\text{GVDW}}[f(\Omega)] = A_{\text{hc}}[f(\Omega)] + (1/2)N \int d\Omega f(\Omega)\psi(\Omega) \quad (4')$$

where

$$\psi(\Omega) = \rho \int d\Omega' f(\Omega') a(\Omega, \Omega') \quad (5')$$

is the mean field felt by a single molecule when it has orientation Ω , and

$$a(\Omega, \Omega') = \int' d\mathbf{r} u_{\text{attr}}(\mathbf{r}; \Omega, \Omega') \quad (6')$$

is the average value of the pair attraction between two molecules having orientations Ω and Ω' . The prime on the \mathbf{r} integral restricts the averaging to those values for which the hard cores, with orientations Ω and Ω' , do not penetrate each other. $f(\Omega)$ denotes the fraction of molecules with orientation Ω : $f(\Omega) = \text{constant} (=1/\int d\Omega)$ for the isotropic state of the liquid. Finally, $A_{\text{hc}}[f(\Omega)]$ is the Helmholtz free energy which would be calculated for a fluid of molecules which interact *only* via hard core (hc) repulsions and whose orientational distribution is $f(\Omega)$. We emphasize that $f(\Omega)$ minimizes the full A , not A_{hc} . Having determined the dependence of A on $f(\Omega)$, T , N , and V (or ρ), the remaining thermodynamic functions follow from the usual partial derivatives: $S = -(\partial A/\partial T)_{V,N,f(\Omega)}$, $P = -(\partial A/\partial V)_{T,N,f(\Omega)}$, and $\mu = (\partial A/\partial N)_{T,V,f(\Omega)}$. Thus a complete specification of the phase transition depends on the choice of A_{hc} and ψ .

It is interesting to note that in the case where the molecular hard cores are allowed to become hard spheres, i.e., all anisotropy in the repulsive forces is neglected, and $u_{\text{attr}}(\mathbf{r}; \Omega, \Omega')$ is taken to have its dispersive (long-range) form, minimization of the $A[f(\Omega)]$ in eq 4'–6' leads^{12a} to a self-consistency relation for $f(\Omega)$ which is identical with that of the familiar Maier–Saupe

theory.³ But instead of a phenomenological parameter specifying the strength of the mean-field potential, we obtain an explicit expression involving the dispersional coefficients, the molecular size, the density, and the temperature.^{12a,45}

Finally, in the case of no attractions ($\psi = 0$) the GVDW theory reduces trivially to the hard-particle theory mentioned earlier.

The calculation of A_{hc} requires a statistical-mechanical theory of dense fluids whose particles interact via nonspherical hard core repulsions. To date, the primary molecular level approach which has been used to determine the functional dependence of A_{hc} on $f(\Omega)$ is the scaled particle theory (SPT) which was originally developed²⁰ to treat fluids of spherical particles. But in the case of liquid crystals it can be shown^{21,22} that thermodynamic inconsistencies arise from application of this theory. Accordingly we were led to consider a completely different approach to the description of the hard-particle reference system.

The Hard-Particle Reference System

The y Expansion for Isotropic States of Hard-Particle Fluids. The idea of expanding thermodynamic functions in powers of quantities other than the density is not new; activity (fugacity) expansions, for example, are well known.²³ Our particular choice of expansion variable arose naturally²⁴ from a critical study²² of the scaled particle theory. But we proceed now by simply defining the quantity

$$y \equiv \frac{\nu_0 \rho}{1 - \nu_0 \rho} \equiv \frac{d}{1 - d} \quad (7)$$

and considering the exact equation of state as an infinite-order power series in y

$$\nu_0 \frac{P}{kT} = \sum_{n=1}^{\infty} C_n y^n = \sum_{n=1}^{\infty} C_n \left(\frac{d}{1-d} \right)^n \quad (8)$$

ν_0 is the hard particle volume.

Assuming the convergence of the usual virial series

$$\nu_0 \frac{P}{kT} = \sum_{n=1}^{\infty} B_n d^n \quad (9)$$

and resumming it into the form of (8), we find

$$C_n = \sum_{k=1}^n \binom{n-1}{k-1} (-1)^{n-k} B_k \quad (10)$$

Thus the first n terms in the y expansion (eq 8) are completely determined by the first n virial coefficients.

Consider first the case of a hard-sphere fluid. Here the values of the first four virial coefficients are known exactly,²⁵ allowing us to determine—via eq 10—the first four C_n ; in addition, B_5 has been evaluated²⁶ by Monte Carlo techniques with sufficient accuracy to provide meaningful determination of the corresponding C_5 . The y expansion is found to converge very quickly, *over the*

(20) H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.*, **31**, 369 (1959); review by H. Reiss in "Statistical Mechanics and Statistical Methods in Theory and Application", V. Landman, Ed., Plenum Press, New York, 1977.

(21) (a) G. Lasher, *J. Chem. Phys.*, **53**, 4141 (1970); (b) R. M. Gibbons, *Mol. Phys.*, **18**, 809 (1970); (c) M. A. Cotter, *Phys. Rev. A*, **10**, 625 (1974); see also ref 8 and 13.

(22) B. Barbov and W. M. Gelbart, *J. Stat. Phys.*, **22**, 685 (1980).

(23) T. L. Hill, "Statistical Mechanics", McGraw-Hill, New York, 1956.

(24) B. Barbov and W. M. Gelbart, *J. Chem. Phys.*, **71**, 3053 (1979).

(25) K. W. Kratky, *Physica*, **87A**, 584 (1977).

(26) F. H. Ree and W. G. Hoover, *J. Chem. Phys.*, **46**, 4181 (1967).

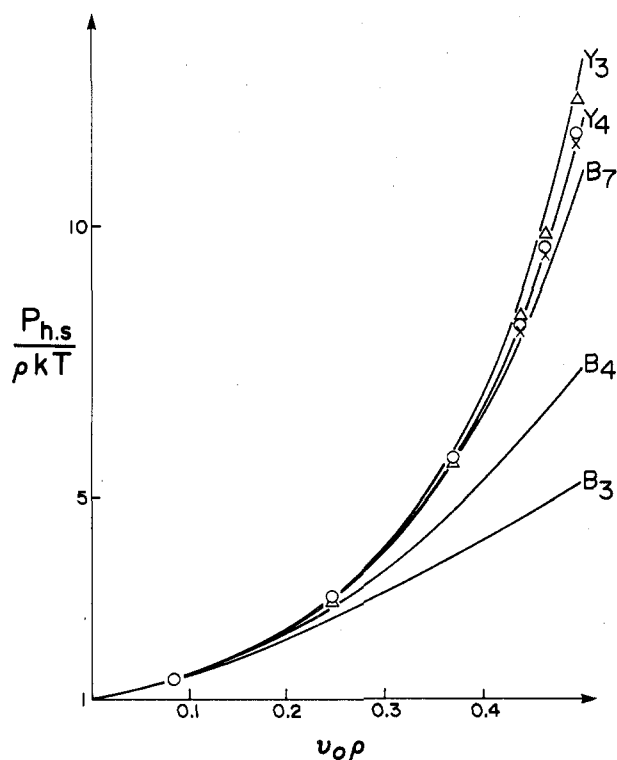


Figure 2. Pressure (P) vs. density (ρ) equation of state for the hard-sphere (hs) fluid; ν_0 is the volume of a single particle. The curves labeled by Y_n and B_n correspond to the n -term truncations of the y expansion and virial series, respectively. (O) Molecular dynamics data;¹⁸ (x) [3,3] Padé approximant;²⁷ (Δ) [4,3] Padé.²⁷

entire fluid range (i.e., $\nu_0\rho \lesssim 0.5$), in marked contrast to the slowly converging virial series. In fact, keeping only three terms in (8) gives (since $C_1 = 1$, $C_2 = 3$, and $C_3 = 3$)

$$\nu_0 \frac{P_{hs}}{kT} = \left(\frac{d}{1-d} \right) + 3 \left(\frac{d}{1-d} \right)^2 + 3 \left(\frac{d}{1-d} \right)^3 \quad (11)$$

an equation of state for hard spheres which is identical with that obtained from the Percus–Yevick (PY)²⁷ and scaled-particle (SP)²⁰ theories! Equation 11 is known to provide a good description of the hard-sphere pressure up to the maximum liquid densities. Thus we expect that keeping an additional term in the y expansion will give an even better equation of state. This is shown in Figure 2 where we plot $P_{hs}/\rho kT$ vs. $\nu_0\rho$ for the three- and four-term truncations (henceforth denoted Y_3 and Y_4) of the series (eq 8). These results are compared there with molecular dynamics (MD) data,¹⁷ Padé approximants,²⁶ and the three, four-, and seven-term truncations of the virial series (B_3 , B_4 , B_7). Note that Y_3 , determined completely by B_1 , B_2 , and B_3 , gives as accurate a pressure as does the [4,3] Padé approximant which requires four additional, higher order virial coefficients.

To test the ability of eq 8 to describe the thermodynamics of reference systems composed of nonspherical particles, consider a fluid of fused-sphere homonuclear dumbbells. For the case considered in Figure 3, Monte Carlo (MC) evaluations of B_3 and B_4 are available,²⁸ so that we can compute simply the three- and four-term

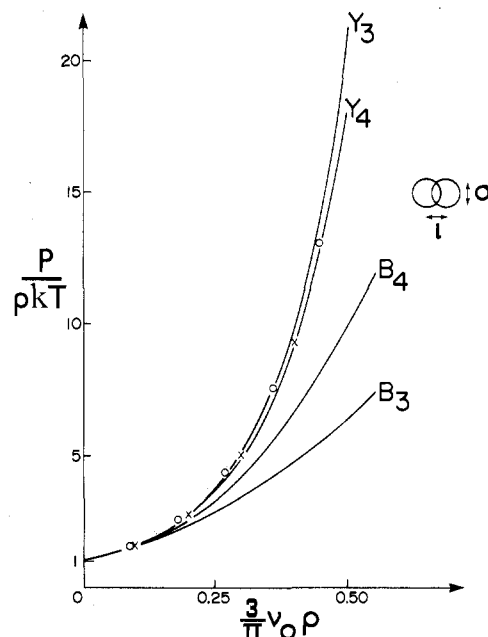


Figure 3. P vs. ρ for fluid of fused-sphere homonuclear dumbbells with $l = 0.6\sigma$. The Monte Carlo data are shown by circles^{29a} and crosses.^{29b}

truncations of the y expansion. Figure 3 compares these results for Y_3 and Y_4 with MC results²⁹ for $P/\rho kT$ and with the corresponding truncated virial series. Again the y expansion converges quickly, with Y_3 and Y_4 bracketing the MC data and providing a better representation of the pressure than do the much more complicated determinations from Percus–Yevick (PY)³⁰ and reference-interaction-site-model (RISM)²⁹ theories.

Many other examples of the Y_3 and Y_4 representation of hard particle fluids and mixtures have been given in our earlier work.²⁴ We have also discussed various improvements and extensions³¹ of this basic starting point. But for our present purpose it suffices to note that Y_3 provides a very good approximation to thermodynamic functions of hard particle liquids and that to do so requires only the second and third virial coefficients. To treat the possibility of long-range orientational ordering, however, we need first to generalize the y expansion to the case of multicomponent systems involving arbitrary nonspherical hard cores. This equation of state describes the thermodynamics of a pure fluid, e.g., liquid crystal, as soon as each of the distinguishable components of the mixture is associated with a different orientation of the nonspherical particle.³²

The y Expansion for Mixtures and Liquid Crystals. The generalization of eq 8 to the case of an M component mixture gives^{24,31}

$$\frac{P}{kT} = \sum_{i_1=0}^{\infty} \dots \sum_{i_M=0}^{\infty} C_{i_1 \dots i_M} \left(\prod_{k=1}^M \frac{y_k^{i_k}}{i_k!} \right) n! \quad (12)$$

Here

$$y_k \equiv \rho_k / (1 - \sum_{l=1}^M \nu_{0l} \rho_l), \quad n \equiv \sum_{k=1}^M i_k, \quad \rho_k \equiv x_k \rho$$

(29) I. Aviram, D. J. Tildesley, and W. B. Streett, *Mol. Phys.*, **34**, 881 (1977); B. C. Freasier, *Chem. Phys. Lett.*, **25**, 280 (1975).

(30) Y. D. Chen and W. A. Steele, *J. Chem. Phys.*, **54**, 703 (1971).

(31) B. Barbooy and W. M. Gelbart, *J. Stat. Phys.*, **22**, 709 (1980).

(32) L. Onsager, *Ann. N.Y. Acad. Sci.*, **51**, 627 (1949).

(27) J. K. Percus and G. J. Yevick, *Phys. Rev.*, **110**, 1 (1958); E. Thiele, *J. Chem. Phys.*, **39**, 474 (1963); M. S. Wertheim, *Phys. Rev. Lett.*, **10**, 321 (1963).

(28) M. Rigby, *J. Chem. Phys.*, **53**, 1021 (1970).

where x_k is the fraction of "k" particles. ν_{0l} is the volume of the l th species' hard core. Note that, when all the species are identical except for each corresponding to a different orientation, we have

$$\nu_{0l} \rightarrow \nu_0 \quad \sum_{l=1}^M \rho_l \rightarrow \rho$$

$$\prod_{k=1}^M \frac{y_k^{i_k}}{i_k!} \rightarrow \left(\frac{\rho}{1 - \nu_0 \rho} \right)^n \prod_{k=1}^M \frac{x_k^{i_k}}{i_k!} \quad (12A)$$

The coefficients $C_{i_1 \dots i_M}$ are given by a generalization of (10):

$$C_{i_1 \dots i_M} = \sum_{j_1=0} \dots \sum_{j_M=0} \frac{m}{n} (-1)^{n-m} B_{j_1 \dots j_M} \prod_{k=1}^M \left(\frac{i_k}{j_k} \right) \nu_{0k}^{i_k - j_k} \quad (13)$$

$$n = \sum_{k=1}^M i_k \quad m = \sum_{k=1}^M j_k$$

The $B_{j_1 \dots j_M}$ are the usual multicomponent-mixture virial coefficients.³³

Equation 12 for the pressure follows, via $P = -(\partial A / \partial A)_{T, N_i, \{x_k\}}$, from the virial expansion for A and relationship 13 between B and C coefficients. Similarly, the chemical potential of the k th species is obtained from $\mu_k = (\partial A / \partial N_k)_{T, V, \{x_j, j \neq k\}}$. From this point on we shall take all particles to have the same nonspherical hard core, each species corresponding to a different orientation. Thus (12A) holds and x_k gives the fraction of molecules having orientation k . In the "continuum limit",³² $x_k \rightarrow x(k) \rightarrow f(\Omega_k) \rightarrow f(\Omega)$ is the usual orientational distribution function. To find the isotropic liquid crystal equilibrium we seek a $\{x_k\}$ [or $f(\Omega)$] and ρ for each phase so that A is minimized subject to equal P and μ .

The Effective Attraction

Recall the definition of the mean field $\psi(\Omega)$, according to eq 5'-6'. This effective attraction, acting separately on each molecule, can be calculated as soon as we specify $u_{\text{attr}}(\mathbf{r}; \Omega, \Omega')$ and the hard-core size and shape. Suppose we have in mind the dispersional interaction between two cylindrically symmetric molecules whose long axes make an angle (Ω_i, Ω_j) with each other. Then

$$u_{\text{attr}}(\mathbf{r}_{ij}; \Omega_i, \Omega_j) = -\frac{C_{\text{iso}}}{r_{ij}^6} - \frac{C_{\text{aniso}}}{r_{ij}^6} \cos^2(\Omega_i, \Omega_j) + \dots \quad (14)$$

where the coefficients C_{iso} and C_{aniso} are related to the average value and difference, respectively, of the molecular polarizability tensor components.³⁴ For physically reasonable values of C_{iso} and C_{aniso} , Gelbart and Gelbart^{12b} have shown that the effective attraction can be expressed to an excellent approximation in the form

$$\psi(\Omega) = -|A_0|\rho - |A_2|\rho\eta P_2(\Omega) \quad (15)$$

where $|A_0|$ and $|A_2|$ are both independent of density and temperature. Here $\eta \equiv \langle P_2(\cos \theta) \rangle \equiv \int d\Omega f(\Omega) P_2(\Omega)$ is the long-range orientational-order parameter, $P_2(\cos \theta) = \frac{3}{2} \cos^2 \theta - \frac{1}{2}$ is the second Legendre polynomial, and θ is the angle between the long molecular axis and the space-fixed, "preferred" direction. At the transition

from isotropic to nematic phases, η changes from zero—since $\langle \cos^2 \theta \rangle = 1/3$ when all θ 's are equally likely—to a value of a few tenths ($\langle \cos^2 \theta \rangle = 1$ and hence $\eta = 1$ only for complete ordering).

Most significantly, it is the isotropic term in u_{attr} which makes the dominant contribution to $|A_2|$, the coefficient of the angle-dependent term in the mean field. This comes about because the anisotropic repulsions build in short-range correlations between the molecular orientations and their separation vector. Recall from eq 5'-6' that the hard core enters via the prime in the mean field averaging which excludes all relative positions denied to a pair of particles by their "shape repulsions" (excluded volume). It is precisely this anisotropy of the molecular cores which allows the $-C_{\text{iso}}/r^6$ term in u_{attr} to dominate the angle dependence in ψ .

Suppose, in fact, that u_{attr} had no anisotropy whatsoever, i.e., it depended only on the distance (r) between centers of mass. Now imagine that we sit on a molecule in the nematic phase and enquire of its average attraction to the other molecules. Because most of its neighbors lie along some preferred direction, this average attraction will be a maximum when the molecule also lies along this direction, for then, given its prolate shape, it will be able to get closer to the others and hence interact more strongly. Conversely if it lies perpendicular, the average attraction will be a minimum. In this way the mean field (ψ) acquires angle dependence from the hard core asymmetry.

Thermodynamic Calculations and Discussion

The above described GVDW theory provides an *a priori* and self-consistent description of the dependence of the isotropic-nematic transition temperature on molecular anisotropy and correctly describes the relative roles of repulsions and attractions in driving the orientational ordering. In particular, it establishes that the average attraction felt by a molecule acquires its orientation dependence primarily from the anisotropy of the hard-core repulsions. The thermodynamic trends found for the isotropic-nematic phase transitions are thereby interpreted in explicit terms of the two sources of local anisotropy: (1) the direct effect of the hard rod repulsions—see $A_{\text{hc}}[f(\Omega)]$ in eq 4'—and (2) their indirect contributions to the angle-dependent part of $\psi(\Omega)$ —see the second term in eq 4'.

By minimization of A_{GVDW} in (4') with respect to $f(\Omega)$, subject to the constraint of equal pressures and chemical potentials, transition temperatures and coexisting densities and $f(\Omega)$'s have been calculated. For spherocylindrical hard cores having length-to-width ratio $x = 3$ and volume $\nu_0 = 230 \text{ \AA}^3$,^{35a} Cotter^{13a} chose the form (15) for $\psi(\Omega)$, set empirically $(\nu_0 k)^{-1}|A_0| = 25000 \text{ K}$ and $(\nu_0 k)^{-1}|A_2| = 2000 \text{ K}$,^{35b} approximated $A_{\text{hc}}[f(\Omega)]$ from SPT, and carried out extensive computations over a wide range of pressure. Whereas quite satisfactory agreement between theory and experiment is achieved for several properties, the calculations dramatically overestimate the strength of the transition: the discontinuities $\Delta\rho/\rho$, ΔS , and ΔH are much too large.

(35) (a) These values of x and ν_0 for PAA are estimated from the known molecular geometry and atomic radii. (b) $(\nu_0 k)^{-1}|A_0|$ were chosen primarily to reproduce the observed temperature and density dependence of η , but $(\nu_0 k)^{-1}|A_0| = 25000 \text{ K}$ is essentially the value which would be estimated from the heat of vaporization for PAA.

(33) J. E. Mayer, *Hand. Phys.*, **12**, (1958).

(34) See, for example, H. Margenau and N. Kestner, "Intermolecular Forces", Pergamon, London, 1969.

Baron and Gelbart^{12c} have also reported numerical evaluations of the GVDW theory for PAA. They used the same x and ν_0 to define the spherocylindrical hard core and the same SPT to express A_{hc} as a function of $f(\Omega)$. But instead of using an empirical choice for $\psi(\Omega)$, they determined it a priori as described above in the previous section. Their results are qualitatively similar to those of Cotter.

By including the appropriate variations in molecular size (ν_0), shape (x), and polarizability characteristics (C_{iso} and C_{aniso}), GVDW predictions have been made of how $T_{transition}$ will vary through different homologous series of compounds.^{12c} At the same time, precisely because the GVDW theory insists on committing itself to a particular choice of pair potential ($u_{hc} + u_{attr}$), its predictions of many phase transition properties cannot be satisfactorily compared with experiment.

For example, it is now well established that the flexibility of the saturated hydrocarbon end chains, e.g., consider PAA (Figure 1) with $OCH_3 \rightarrow OC_nH_{2n+1}$, accounts for the "odd-even" effects observed for a wide variety of homologous series.³⁶ The "zigzag" structure of these end chains and the loss of rigidity as n becomes large cannot be included easily in the GVDW approach. Similarly, it is not uncommon for a small change in substituents to give a huge change in isotropic-nematic and liquid-solid transition temperatures. Replacing a terminal alkoxy by the corresponding alkyl, for example, can cause the complete disappearance of the nematic phase. Such effects have not yet been accounted for by an a priori theory. In fact, prediction of the "loss" of liquid crystallinity requires a comparable level description of the freezing transition, for—as long as there is an anisotropy in the intermolecular potential—all theories of the isotropic-nematic phase transition predict that the liquid crystal phase will eventually appear as the temperature is lowered. Thus it is insufficient to simply describe the lowering of T_{I-N} upon end-group substitution, say, since we must know in addition whether T_{I-N} still lies above (the new) $T_{liq \rightarrow solid}$.

Nevertheless, on the basis of the work discussed in this Account, it is now reasonably well agreed that a liquid crystal is no different from a "simple" molecular liquid insofar as the importance of short-range repulsions is concerned. In both cases a van der Waals approach is natural, leaving us with the problem of developing adequate statistical-mechanical theories for the relevant hard-core reference system. For atomic and simple molecular fluids, the hard sphere is obviously the appropriate choice; this reference system has been thoroughly and successfully investigated by means of several different analytical and numerical methods.³⁷ In the case of liquid crystals, on the other hand, many choices of hard core present themselves, each with different shape and symmetry. Furthermore, even for the simplest hard core—the axially symmetric spherocylinder—serious problems pervade both the analytical and numerical methods which have been used to calculate macroscopic properties. And Monte Carlo evaluations fail completely to obtain a liquid crystal phase.³⁸ Thus there is at present no direct numerical

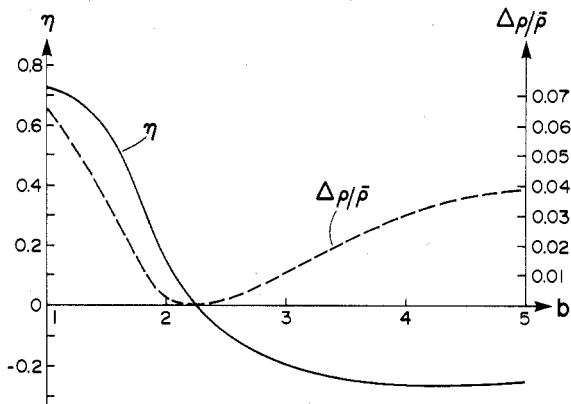


Figure 4. Y_3 results for $\eta_{transition}$ (see left-side ordinate scale) and for $\Delta\rho/\bar{\rho}$ (right side ordinate). The liquid is composed of hard rectangular parallelepipeds with dimensions $a = 1$, b , and $c = 5$.

test of analytical theories of the nematic state.

Equally significant is the fact that even an exact description of the hard-core reference system will not suffice if the particle shape and symmetry are not chosen properly. To date both the scaled particle theories and the computer simulations have only considered molecules which possess cylindrical symmetry. Similarly, the GVDW calculations, and virtually all of the Maier-Saupe-Luckhurst-Chandrasekhar mean-field descriptions, have assumed axial shapes for the liquid crystal forming compounds. Several investigators have suggested, however, that even small deviations from axial symmetry can account for important qualitative features of the isotropic-nematic transition.³⁹⁻⁴¹ To allow for this possibility, recall that we found a " Y_3 " level is sufficient to obtain accurate thermodynamic functions over the full liquid range of densities. Thus we might argue that the first three terms ($n \leq 3$) in eq 12 lead directly to the necessary expressions for the pressure (P_{hc}), Helmholtz free energy (A_{hc}), and chemical potentials ($\{\mu_i\}$). We "simply" need to determine the C coefficients appropriate to the lower-than-axial symmetries of interest.

The problem, of course, is that, even for the simplest possible nonspherical shapes, $B_{n=3}$ (necessary for C_3 —see eq 13) has not been evaluated analytically for arbitrary orientations of the triplets of hard particles. However, if we consider only those orientations for which the principal axes of the particles are coincident with those of a space-fixed reference frame,⁴² then it is straightforward to determine all the relevant expansion coefficients—for many nonspherical shapes. In particular we wish to consider molecules which have lower-than-cylindrical symmetry, i.e., those which are intermediate between rodlike and platelike. To illustrate the effects of symmetry most simply, it is convenient to work with rectangular parallelepipeds having dimensions $a \leq b \leq c$ (with a and c fixed, $c > a$). In the limits $a = b < c$ and $a < b = c$ we recover the rod and plate shapes, respectively. Otherwise ($a \neq b \neq c$) the particles do not have axial symmetry. We search for an isotropic \rightarrow uniaxial phase transition for each value of b and compute the discontinuities in density, $\Delta\rho/\bar{\rho}$,

(36) S. Marcelja, *J. Chem. Phys.*, **60**, 3599 (1974).

(37) See, for example, the review by J. A. Barker and D. Henderson, *Rev. Mod. Phys.*, **48**, 587 (1976).

(38) J. Vieillard-Baron, *Mol. Phys.*, **28**, 809 (1974); J. Kushick and B. J. Berne, *J. Chem. Phys.*, **64**, 1362 (1976).

(39) C. S. Shih and R. Alben, *J. Chem. Phys.*, **57**, 3055 (1972).

(40) J. P. Straley, *Phys. Rev. A*, **10**, 1881 (1974).

(41) G. R. Luckhurst, C. Zannoni, P. L. Nordro, and U. Segre, *Mol. Phys.*, **30**, 1345 (1975).

(42) Suggestions of this kind go back to R. W. Zwanzig, *J. Chem. Phys.*, **39**, 1714 (1967).

and orientational order, $\Delta\eta = \eta_{\text{uniaxial}} \equiv \sum_{k=1}^6 x_k P_2(\cos \theta_k)$, where θ_k is the angle between the space-fixed z direction and the long axis of the particle having orientation k . Note that for principal axes constrained to lie along the space-fixed directions, only six orientations are allowed.⁴³

Figure 4 shows our Y_3 results for η at the transition in the case $a = 1$, $c = 5$, and $a < b < c$. In ref 44 we presented similar results for Y_2 . For $b = 1$, the rod limit, only nematic (long-axis) ordering is possible and η_{trans} is as large as 0.72, almost twice the typical experimental value reported in the literature. The figure also shows our results for $\Delta\rho/\bar{\rho}$: for $b = 1$, $\Delta\rho/\bar{\rho}$ is found to be as large as 0.066, more than ten times the familiarly observed values and comparable to the values found in the GVDW calculations^{12c,13a} mentioned earlier. As b increases, however, the "rod" becomes more platelike and both η_{trans} and $\Delta\rho/\bar{\rho}$ decrease dramatically. For a special intermediate value of $b = b^*$ (≈ 2.25), in fact, both these discontinuities vanish identically. This is the point where the tendencies to form nematic (long-axis-ordered) and planar (short-axis-ordered) uniaxial states become equal. Then, for $b > b^*$ the particles are more platelike than rodlike and it is the short axes which tend to line up in the uniaxial phase. In this case η —the excess fraction of particles whose long axes lie along the preferred direction—is of course negative. Note that the qualitative behavior shown in Figure 4—in particular the zero for some intermediate nonaxial shape—is independent of our choice of particle type (i.e., rectangular parallelepiped vs. ellipsoid, etc.) and of restricted orientations: it follows from general symmetry considerations.

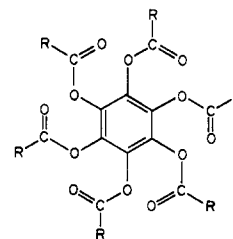
Concluding Remarks

It is clear from Figure 4 why most theory to date, constraining the molecular symmetry to be rodlike, has overestimated the first orderness of the isotropic–nematic transition. Because nature's easiest way to make stable, anisotropic molecules is by conjugating benzene rings, the prototype liquid crystal forming species are those based on cores of biphenyl, azobenzene, azoxybenzene, naphthalene, etc. In all these cases, because of the diameter and thickness of the benzene rings, the molecular shapes correspond to the region of Figure 4 just to the left of b^* .

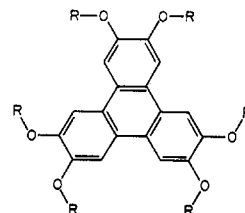
According to the theory presented above, liquids of molecules whose shapes are pure platelike or rodlike should show relatively large discontinuities at the iso-

(43) See, however, J. P. Straley, *J. Chem. Phys.*, **57**, 3694 (1972), and ref 31.

(44) W. M. Gelbart and B. Barbov, *Mol. Cryst. Liq. Cryst.*, **55**, 209 (1979).



(A)



(B)

Figure 5. Schematic drawings of (here $R = C_nH_{2n+1}$) (A) benzene hexa- n -alkanoates and (B) 2,3,6,7,10,11-hexaalkoxytriphenylenes.

tropic uniaxial phase transition. For "plates" this is in fact observed to be the case. (Molecular liquids composed of pure "rods" have not yet been realized.) Chandrasekhar et al.⁴⁵ have, for example, studied benzene derivatives of the form shown in Figure 5A. Using the Clausius–Clayperon equation and their measured values of $\Delta P/\Delta T$ (along the isotropic–discotic equilibrium curve), ΔH , T_{trans} , and the density of the isotropic phase, we find $\Delta V/\bar{V} \approx 0.01$ for the $n = 7$ derivative shown in Figure 5A. The planar liquid crystal phases of other disklike molecules have also been studied,^{46,47} Billard et al.⁴⁶ have measured latent heats at the isotropic–discotic transitions undergone by the compounds shown in Figure 5B. $\Delta P/\Delta T$ data are not yet available for these systems, but the observed ΔH values are ~ 1 – 2 kcal/mol for $n = 5$ and 7 , with corresponding transition temperatures of ~ 380 K. Thus the entropy changes are as large as 3 – 5 cal/(mol K), consistent with the strong first-order phase change expected from our theory.

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(46) J. Billard, J. C. Dubois, N. H. Tinh, and A. Zann, *Nouv. J. Chim.*, **2**, 535 (1978).

(47) A. M. Levelut, *J. Phys., Lett. (Orsay, Fr.)* **40**, 81 (1979); *Mol. Cryst. Liq. Cryst. Lett.*, **49**, 169, 175 (1979).