The Van der Waals Theory of Nematic Liquids [and Discussion]

Martha A. Cotter, J. D. Litster and Lin Lei

Phil. Trans. R. Soc. Lond. A 1983 **309**, 127-144
doi: 10.1098/rsta.1983.0028

Phil. Trans. R. Soc. Lond. A **309**, 127–144 (1983)
Printed in Great Britain

The van der Waals theory of nematic liquids

By Martha A. Cotter
Department of Chemistry, Rutgers – The State University,
New Brunswick, New Jersey 08540, *U.S.A.*

This paper describes the van der Waals theory of nematic liquids, an approximate molecular theory in which very short-range intermolecular repulsions are approximated by hard-rod exclusions, and somewhat longer-ranged intermolecular attractions are subject to a self-consistent mean-field treatment. The rationale, underlying assumptions, idealizations and approximations of the theory are presented in detail and the numerical results so far reported are summarized, together with the results of extensive new calculations, which provide a quite accurate test of the theory in its present state. Finally, the current status of the theory, its relative strengths and weaknesses, and the prospects for extending and improving it are discussed.

1. Introduction

A nematic mesophase is a very complex condensed system for which relatively little is known about the precise form of the intermolecular pair potential. It is therefore clearly impossible to devise a realistic molecular theory of nematogens. Instead, any tractable molecular theory of these systems must incorporate a number of rather severe idealizations or approximations. What sort of idealized model or statistical mechanical approximations to invoke depends on the purpose for which the theory is intended.

At present, the most important aspects of nematic mesomorphism which need to be addressed by molecular theories are (1) the nature of the nematic–isotropic (N–I) and the nematic–smectic A (S–N) phase transitions and (2) the relation between molecular structure and the stability and properties of nematic mesophases. For investigating critical phenomena in the vicinity of the N–I or S–N transition temperatures, the molecular details of the model system are presumably not important as long as the model Hamiltonian has the correct symmetry. On the other hand, it is important that the statistical mechanics be done as accurately as possible. In this case, therefore, one can profitably use a very highly idealized model system such as an array of point particles on a three-dimensional lattice interacting through a nearest-neighbour pair potential $-JP_2(\cos\theta_{ij})$, where J is a positive constant, P_2 is the Legendre polynomial of order 2, and θ_{ij} is the angle between the unit vectors $\boldsymbol{a}_i$ and $\boldsymbol{a}_j$, which characterize the 'orientations' of particles i and j respectively. On the other hand, such a simple model is clearly inadequate for investigating the relation between molecular structure and the stability and properties of nematic phases. For this purpose, a more 'chemical' model is needed, i.e. a model for which it is a relatively straightforward task to build in what is known about the size, shape, flexibility, polarity, polarizability, etc. of a particular nematogen. The van der Waals theory of nematic liquids is intended to be such a 'chemist's' theory. Conversely, it is not designed for the study of critical phenomena in nematogenic systems.

In addition to being a 'chemist's' approach, the van der Waals theory may be viewed as a hybrid of what were once the two rival theoretical approaches to nematogens: (1) the Maier–

Saupe theory (Maier & Saupe 1959, 1960) and its extensions and modifications (see Luckhurst (1979) for a review of Maier–Saupe-type theories) and (2) the so-called 'hard-rod' theories of nematics (see Cotter (1979*a*) for a review of hard-rod theories). In the former it was assumed that nematic order results primarily from the anisotropy of the intermolecular attractions, particularly London dispersion forces, and these attractions were treated in the mean-field approximation. In the latter it was assumed that nematic order results primarily from excluded volume effects, and model systems of hard (i.e. infinitely impenetrable) rod-like objects were therefore used. In the van der Waals theory, the model molecules have hard cores as in hard-rod theories, but they also exhibit anisotropic intermolecular attractions, and the latter are treated in the mean-field approximation. The need for hybrid theories incorporating both anisotropic intermolecular repulsions *and* attractions was made clear over the years by a variety of experimental results.

Finally, the van der Waals theory of nematogens is a historical and logical descendant of the van der Waals theory of simple liquids, which employed a model system of hard spheres in a spatially uniform mean-field arising from intermolecular attractions. This approach was used quite successfully by Longuet-Higgins & Widom (1964) to calculate the thermodynamic properties of liquid argon near its triple point. This success leads one to hope that a similar approach with the use of rod-like molecular hard cores and an orientation-dependent mean field can be used successfully to treat nematic liquids.

The basic assumptions, idealizations and approximations of the van der Waals theory are described in §2 of this paper, and the numerical results so far obtained are summarized in §3. Finally, the current status of the theory and the prospects for improving and extending it are discussed in §4.

2. Basic assumptions, idealizations and approximations

The van der Waals theory of nematic liquids, like the van der Waals theory of simple liquids, is based on three underlying assumptions: (1) that the structure of a liquid far from the gas–liquid critical point is largely determined by very short-ranged intermolecular repulsions; (2) that these repulsions may satisfactorily be approximated by hard-core exclusions; and (3) that the primary role of the somewhat longer-ranged intermolecular attractions (dispersion forces, etc.) is – to a first approximation – to provide a negative, spatially uniform mean field in which the molecules move. For simple liquids, assumptions (1) and (2) are clearly reasonable, since the radial distribution function for liquid argon is barely distinguishable from that of a fluid of hard spheres of appropriate radius. Moreover, the suitability of assumption (3) can be inferred from the success of Longuet-Higgins & Widom's calculations for liquid argon. Since nematic liquids differ from isotropic liquids only in their exhibition of long-range orientational order, it would seem that these underlying assumptions should also be reasonable for nematogens. In practice, of course, applying the van der Waals approach to a nematic liquid is more complicated and risky than applying it to a simple liquid owing to the difficulty in choosing an appropriate shape for the molecular hard cores for a particular nematogen and the necessity to consider molecular orientations as well as positions.

Van der Waals theories of nematics based on rod-like molecular hard cores and an orientation-dependent mean field have been devised by Cotter (1977*a*) and Gelbart & Baron (1977). In the former instance, an empirical mean-field pseudo-potential of the Maier–Saupe type was used. In the generalized van der Waals theory of Gelbart & Baron, on the other hand, the mean-field pseudo-potential was calculated from an assumed intermolecular pair potential in a self-consistent manner. A more compact and straightforward derivation of the generalized van der Waals theory was later presented by Cotter (1977*b*).

In this paper, the statistical mechanical derivation of the van der Waals theory will not be presented, because it is available elsewhere. (The interested reader is referred to the original papers of Gelbart & Baron (1977) and Cotter (1977*a*, *b*) or to the review chapter by Cotter (1979*b*).) Instead, the idealizations and approximations of the theory will be described in detail and the final results of the statistical mechanical manipulations will then be presented.

Without further introduction, therefore, the idealizations and approximations of the van der Waals theory of nematogens are described below.

1. Molecular flexibility is neglected; i.e. the dependence of the potential energy of the system on the intramolecular conformational coordinates of the molecules is neglected and a nematogen is modelled as an inflexible object with some average or effective shape. The potential energy of interaction between two molecules i and j is thus assumed to depend only on the orientations Ω_i and Ω_j of the two molecules and on the vector $\boldsymbol{r}_{ij}$ between their centres. Specifically, the N-body potential energy is assumed to be additive pairwise and the intermolecular pair potential v is assumed to have the form

$$v(\boldsymbol{r}_{ij}, \Omega_i, \Omega_j) = v_{\text{rep}}(\boldsymbol{r}_{ij}, \Omega_i, \Omega_j) + v_{\text{att}}(\boldsymbol{r}_{ij}, \Omega_i, \Omega_j), \tag{1}$$

where v_{rep} is a very short-range repulsive potential and v_{att} is a somewhat longer-ranged attractive potential.

2. The very short-range intermolecular repulsions are approximated by hard-core exclusions; i.e. it is assumed that

$$\begin{aligned} v_{\text{rep}}(\boldsymbol{r}_{ij}, \Omega_i, \Omega_j) &= v^*(\boldsymbol{r}_{ij}, \Omega_i, \Omega_j) \\ &= \begin{cases} \infty & \text{if the hard cores of } i \text{ and } j \text{ would overlap;} \\ 0 & \text{otherwise.} \end{cases} \end{aligned}$$

3. The rod-like molecular hard cores are taken to have cylindrical symmetry. Ω thus represents a set of two angles, the polar angle θ and the azimuthal angle ϕ, which specify the orientation of a cylindrical molecular axis with respect to a space-fixed coordinate system.

4. Intermolecular attractions are treated via the mean-field approximation; i.e. the attractions between a molecule with orientation Ω and all the other molecules are approximated collectively by the interaction of the given molecule with a spatially uniform mean field described by the pseudo-potential $\overline{\psi}(\Omega, \rho)$. As noted above, two different approaches have been used to evaluate the pseudo-potential $\overline{\psi}(\Omega, \rho)$.

(*a*) In the empirical approach first used by Cotter (1977*a*), the pseudo-potential was assumed to have the simple functional form

$$\overline{\psi}(\Omega, \rho) = -v_0\rho - v_2\rho\eta_2 P_2(\cos\theta), \tag{2}$$

where ρ is the number density, v_0 and v_2 are positive constants, θ is the angle between the cylindrical axis of the molecular hard core and the nematic director (taken to be parallel to the z axis of the space-fixed coordinate system), P_2 is the Legendre polynomial of order 2, and η_2, the traditional nematic order parameter, is the average value of $P_2(\cos\theta)$. From a statistical mechanical point of view,

$$\eta_2 = \int f(\Omega)\, P_2(\cos\theta)\, \mathrm{d}\Omega, \tag{3}$$

where $f(\Omega)$ is the normalized one-body orientational distribution function formally defined by the statement that $f(\Omega)\,\mathrm{d}\Omega$ is the fraction of molecules with orientations between Ω and $\Omega+\mathrm{d}\Omega$. In this approach, v_0 and v_2 are treated as adjustable parameters and no attempt is made to calculate the ratio v_2/v_0 from an assumed intermolecular pair potential. Finally, it should be noted that the linear dependence of $\bar{\psi}$ on ρ is required for statistical mechanical self-consistency (Cotter 1977*c*).

(*b*) In the generalized van der Waals theory of Gelbart & Baron (1977), the mean-field pseudo-potential $\bar{\psi}$ is related to the intermolecular pair potential by the equation

$$\begin{aligned}\bar{\psi}(\Omega,\rho) &= \rho\int \mathrm{d}\Omega' f(\Omega')\int \mathrm{e}^{-\beta v^*(\boldsymbol{r},\Omega,\Omega')}\,v_{\mathrm{att}}(\boldsymbol{r},\Omega,\Omega')\,\mathrm{d}\boldsymbol{r}\\ &\equiv \rho\int \mathrm{d}\Omega' f(\Omega')\,I(\Omega,\Omega'),\end{aligned} \tag{4}$$

where $\beta = 1/kT$ (k is Boltzmann's constant) and $\boldsymbol{r}$ is the vector connecting the centres of two molecules with orientations Ω and Ω' respectively. Since v^* can have only two values, zero or infinity, the Boltzmann factor $\mathrm{e}^{-\beta v^*}$ serves only to exclude from the range of integration over $\boldsymbol{r}$ all values of $\boldsymbol{r}$ that correspond to overlap of the hard cores of the two given molecules. It is therefore clear that in evaluating $\bar{\psi}$, all short-range correlations between pairs of molecules are neglected *except* for the requirement that their hard cores not overlap.

5. The contribution of the molecular hard cores to the free energy of the system is calculated by using scaled particle theory, an approximate statistical mechanical theory of fluids of hard particles. (See below for an outline of this approach.)

Having made assumptions 1–4 above, it can be shown that the Helmholtz free energy functional for the model system is given by

$$N^{-1}A\{f(\Omega)\} = N^{-1}A^*\{f(\Omega)\} + \tfrac{1}{2}\int f(\Omega)\,\bar{\psi}(\Omega)\,\mathrm{d}\Omega, \tag{5}$$

where $A^*\{f(\Omega)\}$ is the free energy functional for a system of hard rods constrained to have orientational distribution function $f(\Omega)$. The most convenient cylindrically symmetric shape to choose for the molecular hard cores is a spherocylinder (i.e. a right circular cylinder capped on each end by a hemisphere of the same radius) because the mutual exclusion volume of two spherocylinders has a particularly simple dependence on their orientations. One is then confronted by the task of evaluating the Helmholtz free energy of a fluid of hard spherocylinders. This clearly cannot be done exactly. Furthermore, no computer simulation of a system of three-dimensional hard rods, spherocylindrical or otherwise, has succeeded in observing a nematic phase. (There have been successful Monte Carlo simulations for isotropic fluids of hard spherocylinders (see below), but at the high densities apparently required to observe the nematic phase, convergence of the Monte Carlo computations becomes impracticably slow.) Thus some approximate statistical mechanical method must be used to evaluate $A^*\{f(\Omega)\}$. As noted above, in the work so far on the van der Waals theory, the approach used has almost always been scaled particle theory.

Scaled particle theory is an approximate statistical mechanical theory of fluids of hard particles first developed by Reiss *et al.* (1959) to treat systems of hard spheres. For fluids of both hard spheres and hard discs, its predictions agree very well with the results of Monte Carlo and molecular dynamics computer simulations. The theory has been extended to treat systems of hard spherocylinders by a number of authors (Cotter & Martire 1970*a*, *b*; Lasher 1970; Timling 1974;

Cotter 1974, 1977*a*). Although the precise mathematical expressions derived for $A^*\{f(\Omega)\}$ differ somewhat among these various versions of the theory, the numerical results obtained differ very little. In what follows, the version of Cotter (1977*a*) will be discussed for concreteness.

In this version, the central quantity of scaled particle theory for a fluid of hard spherocylinders of radius a and cylindrical length l is the work function $W(\alpha, \lambda, \Omega)$, which is defined as the reversible work necessary to add a scaled spherocylinder of radius αa, cylindrical length λl, and orientation Ω to the system at an arbitrary fixed point. This quantity is related to the chemical potential of the system by the exact relation

$$\mu - \mu_{\text{ideal}} = kT\int f(\Omega)\ln[4\pi f(\Omega)]\,\mathrm{d}\Omega + \int f(\Omega)\,W(1,1,\rho)\,\mathrm{d}\Omega. \tag{6}$$

Although an exact expression for $W(\alpha, \lambda, \Omega)$, valid for all α and λ, cannot be derived, the exact limiting behaviour of W is known for very small and very large scaled spherocylinders, i.e.

$$\lim_{\substack{\alpha\to 0\\ \lambda\to 0}} W(\alpha,\lambda,\Omega) = -kT\ln(1-v_0\rho),$$

where $v_0 = \pi a^2 l + \frac{4}{3}\pi a^3$ is the volume of a hard spherocylinder, and

$$\lim_{\substack{\alpha\to \infty\\ \lambda\to \infty}} W(\alpha,\lambda,\Omega) = P\{\pi(\alpha a)^2\lambda l + \tfrac{4}{3}\pi(\alpha a)^3\},$$

where P is the external pressure. (The latter limit simply recognizes the fact that when the scaled spherocylinder becomes very large, W must equal the reversible thermodynamic work of building a macroscopic cavity in the fluid.) Between these two limits, one approximates $W(\alpha, \lambda, \Omega)$ by using the interpolation formula

$$\begin{aligned} W(\alpha,\lambda,\Omega) = {} & -\ln(1-v_0\rho) + C_{10}(\Omega,a,l,\rho)\,\alpha + C_{01}(\Omega,a,l,\rho)\,\lambda \\ & + C_{11}(\Omega,a,l,\rho)\,\alpha\lambda + C_{20}(\Omega,a,l,\rho)\,\alpha^2 + (\pi a^2 l\beta P)\,\alpha^2\lambda + (\tfrac{4}{3}\pi a^3\beta P)\,\alpha^3, \end{aligned} \tag{7}$$

where $C_{ij} = (i!j!)^{-1}(\partial^{(i+j)}\beta W/\partial\alpha^i\partial\lambda^j)_{\alpha=0,\lambda=0}$. (The derivatives needed to calculate C_{10}, C_{01}, C_{11} and C_{20} can be evaluated exactly.) The equilibrium thermodynamic properties of the system can then be obtained from $\overline{W}(1,1) = \int f(\Omega)\,W(1,1,\Omega)\,\mathrm{d}\Omega$. When the equation of state obtained in this manner for an isotropic fluid of hard spherocylinders is compared with that calculated from computer simulations (Vieillard-Baron 1974; Monson & Rigby 1978), it is found that the agreement is quite good at low to moderate densities, but that the scaled particle predictions for $Pv_0/(kT)$ become significantly and increasingly too large at reduced densities $(v_0\rho)$ of order 0.50. For example, for the highest reduced densities at which the computer simulations were carried out for spherocylinders with length:width ratio $x = 3$ (Vieillard-Baron 1974), namely $v_0\rho = 0.50$ and $v_0\rho = 0.54$, the scaled particle results are too high by 17.3 % and 23.5 % respectively. For spherocylinders with $x = 2$, on the other hand, the highest reduced density considered in the computer simulations (Monson & Rigby 1978) was $v_0\rho = 0.5096$, and the scaled particle prediction is too high by 7.9 % at that point. These discrepancies between theory and computer 'experiment' for the isotropic phase at high densities suggest that the use of scaled particle theory may be a significant source of error in the van der Waals theory. Finding a more accurate but tractable method of evaluating $A^*\{f(\Omega)\}$ is, however, a quite difficult task.

When the expression for $A^*\{f(\Omega)\}$ derived from this version of scaled particle theory is inserted in (5), the final result for the van der Waals free energy functional is

$$\begin{aligned} \frac{A^*\{f(\Omega)\}}{NkT} = {} & \langle\ln\{4\pi f(\Omega)\}\rangle + \ln\{\rho/(1-v_0\rho)\} + \frac{(4+q-\frac{1}{2}q^2)\,(v_0\rho)^2}{3(1-v_0\rho)^2} \\ & + \tfrac{1}{2}\lambda(a,l,\rho)\,\langle\langle|\sin\gamma(\Omega,\Omega')|\rangle\rangle + (2kT)^{-1}\int f(\Omega)\,\overline{\psi}(\Omega)\,\mathrm{d}\Omega, \end{aligned} \tag{8}$$

where

$$\left.\begin{aligned} q = \frac{4\pi a^3}{3v_0}, \quad r = \frac{al^2}{v_0}, \quad \lambda &= \frac{4rv_0\rho\{1-\frac{1}{3}(1-q)\,v_0\rho\}}{(1-v_0\rho)^2}, \\ \langle \ln\{4\pi f(\Omega)\}\rangle &= \int f(\Omega)\ln\{4\pi f(\Omega)\}\,\mathrm{d}\Omega, \\ \langle\langle|\sin\gamma|\rangle\rangle &= \iint |\sin\gamma(\Omega,\Omega')|\,f(\Omega)\,f(\Omega')\,\mathrm{d}\Omega\,\mathrm{d}\Omega', \end{aligned}\right\} \tag{9}$$

and $\gamma(\Omega, \Omega')$ is the angle between directions Ω and Ω'. The orientational distribution function, $f(\Omega)$, is obtained by minimization of the free energy functional. The result is the nonlinear integral equation

$$f(\Omega) = C\exp\left[-\left\{\beta\bar{\psi}(\Omega,\rho)+\lambda(a,l,\rho)\int\mathrm{d}\Omega' f(\Omega')\,|\sin\gamma(\Omega,\Omega')|\right\}\right], \tag{10}$$

where C is a normalization factor.

3. Summary of results

(*a*) *Results obtained by using an empirical pseudo-potential*

Cotter (1977*a*) carried out extensive calculations for a model system with hard-core length: width ratio $x = l/2a+1 = 3$ and compared the results with experimental data for the much-studied nematogen *p*-azoxyanisole (PAA). The hard-core volume v_0 was taken to be 0.230 nm^3 and the mean field pseudo-potential was assumed to have the form (2) with $v_0/(v_0 k) = 25\,000\,\mathrm{K}$ and $v_2/(v_0 k) = 2000\,\mathrm{K}$. The choices for x and v_0 were suggested by Vieillard-Baron (1974), based on estimates from tabulated bond lengths and van der Waals radii. On the other hand, the parameters v_0 and v_2 were chosen to reproduce the experimental values of the transition temperature T_{NI} and the quantity $\tau = -\rho(\partial\eta_2/\partial\rho)_T/T(\partial\eta_2/\partial T)_\rho$ at T_{NI} for PAA. (The latter is a measure of the relative sensitivity of the order parameter η_2 to changes in ρ against changes in T.) In addition to those described above, one further approximation was introduced, namely

$$\langle\langle|\sin\gamma(\Omega,\Omega')|\rangle\rangle \approx \tfrac{1}{4}\pi - \tfrac{5}{32}\pi\eta_2^2, \tag{11}$$

which is obtained by expanding $|\sin\gamma|$ in even-order Legendre polynomials $P_{2n}(\cos\gamma)$, averaging term by term, and then truncating the resulting series after its second term. This should be a reasonably good approximation for relatively small values of η_2, but not for values of η_2 close to unity. For hard spherocylinders with $x = 3$, it lowers the predicted values of the order parameter η_2 by roughly 25 % but changes only slightly the densities of the coexisting phases at the N–I transition. It greatly simplifies the integral equation (10) for $f(\Omega)$, which becomes

$$f(\Omega) = C\exp\{A(\rho,T)\,\eta_2 P_2(\cos\theta)\} = \frac{\exp\{A(\rho,T)\,\eta_2 P_2(\cos\theta)\}}{2\pi\int_0^\pi \exp\{A(\rho,T)\,\eta_2 P_2(\cos\theta)\}\sin\theta\,\mathrm{d}\theta}, \tag{12}$$

where

$$A(\rho,T) = \tfrac{5}{32}\pi\lambda(a,l,\rho) + v_2/kT. \tag{13}$$

Determination of $f(\Omega)$ thus reduces to solving iteratively for η_2 by using the self-consistency condition

$$\eta_2 = \int f(\Omega)\,P_2(\cos\theta)\,\mathrm{d}\Omega = \frac{\int_0^\pi P_2(\cos\theta)\exp[A(\rho,T)\,\eta_2 P_2(\cos\theta)]\sin\theta\,\mathrm{d}\theta}{\int_0^\pi \exp[A(\rho,T)\,\eta_2 P_2(\cos\theta)]\sin\theta\,\mathrm{d}\theta}. \tag{14}$$

To summarize the results of these calculations, it can be said that quite satisfactory qualitative but not quantitative agreement with experiment was obtained. The theory predicts η_2–T curves (at constant P or constant ρ) of roughly the correct shape, nearly linear plots of $\ln T$ against $\ln \rho$ at constant η_2 with slopes close to 4 (in agreement with the data of McColl & Shih (1972)), increases in T_{NI} with increasing P of the correct order of magnitude, and large pre-transitional increases in the compressibility, expansivity and specific heat as T_{NI} is approached from below. (For more details, see Cotter (1977*a*).) On the other hand, the N–I phase transition is predicted to be much too strongly first-order, as can be seen from the first two columns of table 1.

Table 1. Values of various quantities at the N–I phase transition as predicted by the van der Waals theory with the empirical mean field potential

$$\bar{\Psi}(\Omega, \rho) = -\upsilon_0 \rho - \upsilon_2 \rho \eta_2 P_2(\cos\theta)$$

(P = 1 atm (*ca.* 10^5 Pa) in all cases.)

quantity	experimental data for PAA†	theoretical predictions $x = 3$‡	$x = 1.75$‡	$x = 1.75$§
$\{\upsilon_0/(v_0 k)\}/10^4$ K	—	2.50	5.42	5.38
υ_2/υ_0	—	0.0800	0.0326	0.0324
$T_{\mathrm{NI}}/\mathrm{K}$	409	410	409	409
$v_0 \rho_{\mathrm{nem}}$	0.62	0.445	0.62	0.62
$\Delta\rho/\rho_{\mathrm{nem}}$	0.0035	0.040	0.0057	0.0070
$\Delta S/(Nk)$	0.17	0.887	0.508	0.62
η_2	0.36	0.542	0.455	0.499
τ	4.0	3.9	3.9	3.9
$(\mathrm{d}T_{\mathrm{NI}}/\mathrm{d}P)_{P=1\ \mathrm{atm}}/(\mathrm{K/kbar}\Vert)$	48	175	30	31

† For the references from which these values were taken, see Savithramma & Madhusudana (1982*b*).
‡ Calculated by using a two-term expansion of $\langle\langle|\sin\gamma|\rangle\rangle$.
§ Calculated by using a six-term expansion of $\langle\langle|\sin\gamma|\rangle\rangle$.
‖ 1 kbar = 10^5 Pa.

Significantly better agreement with experimental data for PAA can be obtained by using length:width ratios less than 3, as was shown by Savithramma & Madhusudana (1980), who considered various model systems with $x = 1.0$ to $x = 2.45$. They again assumed that $v_0 = 0.230\,\mathrm{nm}^3$ but chose values of υ_0 and υ_2 at each value of x to reproduce the experimental values of T and $v_0\rho_{\mathrm{nem}}$ at the N–I transition. Best results were obtained for $x = 1.75$; these values are given in column 2 of table 1. As can be seen, the overall agreement between theory and experiment is rather good.

Finally, Savithramma & Madhusudana (1982*b*) recently redid their calculations with the truncated two-term expansion for $\langle\langle|\sin\gamma|\rangle\rangle$ replaced by the first six terms in the exact expansion of this quantity. Their results for a system with $x = 1.75$ are given in column 4 of table 1. As can be seen, including the higher order terms in the expansion of $\langle\langle|\sin\gamma|\rangle\rangle$ increases $\Delta\rho/\rho_{\mathrm{nem}}$, η_2, and $\Delta S/Nk$ by 23, 9.7 and 22 % respectively, but agreement with experiment is still rather good. In addition to determining the properties of model systems with various values of x at P = 1 atm (*ca.* 10^5 Pa), they also calculated the properties of a system with $x = 1.75$ for pressures up to 650 MPa and obtained semiquantitative agreement with experimental data on PAA at high pressures.

(*b*) *Results from the generalized van der Waals theory*

As noted previously, the expression for $\bar{\Psi}(\Omega, \rho)$ in the generalized van der Waals theory is (4). Evaluation of the integral $\mathrm{I}(\Omega, \Omega')$ in this equation is a rather formidable problem in solid geometry because it requires the characterization of the surface $S(\gamma)$ that separates the allowed and forbidden values of the vector $\boldsymbol{r}$ between the centres of two molecules with orientations Ω and Ω' respectively (i.e. $S(\gamma)$ is the surface traced out by the centre of a hard spherocylinder with fixed orientation Ω' as it moves about another hard spherocylinder with fixed orientation Ω in such a way that the two particles are always in contact). $S(\gamma)$ was characterized analytically by Gelbart & Gelbart (1977), who then evaluated $I(\gamma)$ numerically for a range of values of the dimensions a and l of the spherocylindrical hard cores.

The first numerical test of the generalized van der Waals approach was reported by Baron & Gelbart (1977), who considered model systems with hard-core length: width ratios x in the range 1.0–4.2 and with attractive potentials

$$v_{\text{att}}(r,\gamma) = -C_{\text{iso}}/r^6 - C_{\text{aniso}}\cos^2(\gamma)/r^6, \tag{15}$$

where C_{iso} and C_{aniso} are positive constants. To avoid solving the nonlinear integral equation (10), they introduced two new approximations, namely

$$f(\Omega) = \cosh(\alpha\cos\theta)\Big/\int_0^\pi \cosh(\alpha\cos\theta)\sin\theta\,\mathrm{d}\theta, \tag{16}$$

where α is determined by minimization of the free energy, and

$$\langle\langle I(\gamma)\rangle\rangle = A_0 + A_2\eta_2^2. \tag{17}$$

Equation (16) is a one-parameter variational approximation for $f(\Omega)$ first suggested by Onsager (1949); (17) is obtained by expanding $I(\gamma)$ in even-order Legendre polynomials, averaging term by term, and then truncating the resulting series after its second term. Gelbart & Gelbart (1977) showed that the latter is a good approximation *if* (16) is valid and η_2 is of order 0.5. However, the very large values of η_2 actually obtained by Baron & Gelbart cast considerable doubt on the validity of this truncation. More importantly, the use of the Onsager approximation (16) clearly introduced substantial error into the calculations, as can be seen by comparing Baron & Gelbart's results for hard spherocylinders with $x = 3$ at the N–I transition ($\eta_2 = 0.96$, $v_0\rho_{\text{nem}} = 0.707$) with the corresponding numbers obtained by Cotter (1979*a*) with the use of the numerical solution of the scaled particle integral equation for $f(\Omega)$ ($\eta_2 \approx 0.64$, $v_0\rho_{\text{nem}} \approx 0.55$). Thus although Baron & Gelbart reported some interesting trends in T_{NI}, ΔS_{NI} and the densities of the coexisting phases at T_{NI} as v_0, x and C_{iso} are varied, it is clear that their results do not constitute a definitive test of the generalized van der Waals theory. Further calculations with a more accurate representation of $f(\Omega)$ were clearly needed.

To provide a more accurate test of the generalized van der Waals approach, I have quite recently carried out a series of calculations based on model systems with hard-core length: width ratios, x, of 1.5, 2.0 and 3.0, and intermolecular attractive potentials with the simple form

$$v_{\text{att}} = -\epsilon_0/r^6 - \epsilon_2 P_2(\cos\gamma)/r^6 = -\epsilon_0\{1+\delta P_2(\cos\gamma)\}/r^6, \tag{18}$$

where ϵ_0 and ϵ_2 are positive constants and $\delta = \epsilon_2/\epsilon_0$. The results are reported here for the first time.

With this choice for v_{att}, the integral equation (10) can be written

$$\ln f(\Omega) = \ln C - \int \mathrm{d}\Omega' f(\Omega')\{\lambda(a,l,\rho)\,|\sin\gamma(\Omega,\Omega')| + (\rho/kT)\,I(\Omega,\Omega')\}, \tag{19}$$

where

$$I(\Omega,\Omega') = I(\gamma) = -\epsilon_0\{1+\delta P_2(\cos\gamma)\}\int \mathrm{e}^{-\beta v^*(r,\gamma)}r^{-6}\,\mathrm{d}\boldsymbol{r}$$

$$\equiv -\epsilon_0\{1+\delta P_2(\cos\gamma)\}\,I_0(\gamma). \tag{20}$$

This nonlinear integral equation was solved numerically by expanding $\ln f(\Omega)$ in even-order Legendre polynomials through $P_{20}(\cos\theta)$, i.e. by assuming that

$$\ln f(\Omega) = \sum_{n=0}^{10} F_n P_{2n}(\cos\theta), \tag{21}$$

and solving iteratively for the coefficients F_0 to F_{10}. This requires knowing the first 11 coefficients in the Legendre expansions of $|\sin\gamma|$ and $I_0(\gamma)$, i.e. the first 11 coefficients B_n and D_n, where

$$|\sin\gamma| = \sum_{n=0}^{\infty} B_n P_{2n}(\cos\gamma) \tag{22}$$

and

$$I_0(\gamma) = \sum_{n=0}^{\infty} D_n P_{2n}(\cos\gamma). \tag{23}$$

The B_n are easily determined analytically; the D_n were obtained by numerical integration with the use of the two-dimensional integral representation of $I_0(\gamma)$ derived by Gelbart & Gelbart (1977). To calculate the reduced density $v_0\rho$ and the coefficients F_n at a particular temperature T and external pressure P_{ext}, one can solve (19) simultaneously with

$$\Pi(T, v_0\rho) = P_{\text{ext}} v_0/kT, \tag{24}$$

where $\Pi(T, v_0\rho)$ is the van der Waals expression for Pv_0/kT, namely

$$\Pi = \frac{v_0\rho[1+v_0\rho+\frac{2}{3}(v_0\rho)^2(1+q-\frac{1}{2}q^2)+2rv_0\rho\{1+\frac{1}{3}(1+2q)v_0\rho\}\langle\langle|\sin\gamma|\rangle\rangle]}{(1-v_0\rho)^3} - \frac{\epsilon_0(v_0\rho)^2}{2v_0kT}\langle\langle I(\gamma)\rangle\rangle. \tag{25}$$

Convergence of the iterative procedure is, however, rather slow. Much faster convergence can be obtained by fixing P_{ext} and the coefficient F_1 (rather than P_{ext} and T) and solving for T, $v_0\rho$ and the remaining F_n by using (19), (24) and the exact relation

$$F_1 = -\{\lambda(a, l, \rho)B_1 + \rho D_1/kT\}\eta_2. \tag{26}$$

(This can be derived by substituting the Legendre expansions for $\ln f(\Omega)$, $|\sin\gamma|$, and $I(\gamma)$ in (19), integrating over Ω' term by term, and then equating the coefficients of $P_2(\cos\theta)$ on each side of the resulting equation.) The latter was the procedure actually used in the computations. Once the values of F_2 to F_{10}, η_2 to η_{20}, $v_0\rho$ and T were determined for a nematic phase with the specified P and F_1, the chemical potential μ, entropy S, Helmholtz free energy A, and internal energy U were calculated. Equation (25) with $\langle\langle|\sin\gamma|\rangle\rangle = B_0 = \frac{1}{4}\pi$ and $\langle\langle I(\gamma)\rangle\rangle = D_0$ was then solved iteratively for the density of an isotropic phase with the same T and P as the nematic phase in question and μ, S, A and U were calculated for this isotropic phase. The N–I phase transition was located by searching for the value of F_1 such that μ_{nem} and the corresponding μ_{iso} are equal. Finally, the quantity $\tau = -\rho(\partial\eta_2/\partial\rho)_T/T(\partial\eta_2/\partial T)_\rho$ was evaluated by numerical differentiation and $(\mathrm{d}T_{\text{NI}}/\mathrm{d}P)_{P=1\,\text{atm}}$ was evaluated by using the Clausius–Clapeyron equation. The results obtained in this manner are summarized in tables 2–4.

The properties of three model systems with $x = 1.5$, 2 and 3 respectively at the N–I transition at $P = 1$ atm are given in table 2. In each case, v_0 was taken to be 0.230 nm^3, ϵ_2 was set equal to zero (i.e., v_{att} was taken to be isotropic) and ϵ_0 was chosen to obtain an N–I transition temperature of approximately 409 K. The relevant experimental data for PAA are again given for purposes of comparison. As can be seen, the agreement with experiment is atrociously poor when $x = 3$, still rather poor when $x = 2$, and respectable, but not terribly impressive, when $x = 1.5$. Clearly, in

Table 2. Values of various quantities at the N–I phase transition as predicted by the generalized van der Waals theory with $v_{\mathrm{att}} = -\epsilon_0/r^6$

($P = 1$ atm in all cases.)

quantity	experimental data for PAA	theoretical predictions $x = 3$	$x = 2$	$x = 1.5$
$\{v_0/(kv_0 a^3)\}/10^4$ K	—	7.60	7.73	10.7
$T_{\mathrm{NI}}/\mathrm{K}$	409	408.6	408.4	408.8
$v_0\,\rho_{\mathrm{nem}}$	0.62	0.450	0.456	0.559
$\Delta\rho/\rho_{\mathrm{nem}}$	0.0035	0.481	0.116	0.015
$\Delta S/(Nk)$	0.17	6.99	2.65	1.07
η_2	0.36	0.974	0.816	0.607
η_4	0.07	0.919	0.572	0.284
τ	3.9	1.61	1.65	1.64
$(\mathrm{d}T_{\mathrm{NI}}/\mathrm{d}P)_{P=1\,\mathrm{atm}}/(\mathrm{K/kbar})$	48	497	184	44

its present form the generalized van der Waals theory greatly exaggerates the degree of orientational order in the nematic phase and the strength of the first-order N–I transition, even when an *isotropic* attractive potential v_{att} is used. The mathematical origins of this behaviour can be inferred from table 3, which lists the values of the coefficients F_n in the expansion of $\ln f(\Omega)$, the order parameters η_{2n}, and the coefficients D_n in the expansion of $I(\gamma)$ for these three model systems. When $\delta = 0$, the mean field pseudo-potential is given by

$$\overline{\psi}(\Omega,\rho) = -\rho\epsilon_0 \int f(\Omega')\,I_0(\gamma)\,\mathrm{d}\Omega'$$

$$\approx -\rho\epsilon_0 \sum_{n=0}^{10} D_n \eta_{2n} P_{2n}(\cos\theta). \tag{27}$$

It is therefore clear that the pseudo-potentials calculated from the generalized van der Waals theory are much more strongly orientation dependent than the sort of empirical $\overline{\psi}$'s that yield the best agreement with experiment. This very strong favouring of alignment results in large values of the order parameters η_2, η_4, etc., in the nematic phase and these high order parameters, together with the relatively large values of D_2, D_4, etc., yield large order-dependent terms in the internal energy U of the system. To be slightly more quantitative, let us define an anisotropy parameter by the relation

$$\xi = \{U(1) - U(0)\}/U(0), \tag{28}$$

where $U(1)$ and $U(0)$ are, respectively, the internal energies of a perfectly ordered nematic phase and of an isotropic phase at density ρ and temperature T. For the three model systems described in tables 2 and 3, with $x = 3$, 2 and 1.5, the values of ξ are 0.679, 0.365 and 0.133 respectively. On the other hand, for the model systems described in table 1 (with empirical pseudo-potentials), $\xi = 0.080$ ($x = 3$) and $\xi = 0.032$ ($x = 1.75$).

The effects of adding an anisotropic term proportional to $P_2(\cos\gamma)$ to v_{att} can be seen in table 4, which compares model systems with $x = 1.5$ and four values of δ: 0, 0.01, 0.05 and 0.10. In each case, ϵ_0 was chosen to yield $T_{\mathrm{NI}} \approx 409$ K. From this table it is clear that, on the whole, the agreement between theory and experiment becomes worse as δ increases. This is not surprising because the van der Waals mean field potential is already too strongly orientation-dependent when $\delta = 0$.

TABLE 3. THE COEFFICIENTS F_n AND D_n AND THE ORDER PARAMETERS η_{2n} FOR THE MODEL SYSTEMS IN TABLE 2

(F_n is the coefficient of $P_{2n}(\cos\theta)$ in the Legendre expansion of $\ln f(\Omega)$ and D_n is the coefficient of $P_{2n}(\cos\gamma)$ in the Legendre expansion of $I(\gamma)$.)

	$x = 3$			$x = 2$			$x = 1.5$		
n	F_n	a^3D_n	η_{2n}	F_n	a^3D_n	η_{2n}	F_n	a^3D_n	η_{2n}
0	—	0.16984	1.00000	—	0.22688	1.00000	—	0.30499	1.00000
1	5.8219	0.04191	0.97429	3.83640	0.04234	0.81598	2.69633	0.02556	0.60653
2	2.47460	0.02554	0.91931	0.95666	0.01666	0.57174	0.32925	0.00682	0.28467
3	1.32693	0.01582	0.84305	0.29929	0.00836	0.36157	0.05784	0.00299	0.11364
4	0.76661	0.01044	0.75404	0.10373	0.00494	0.21295	0.01166	0.00167	0.04081
5	0.46425	0.00730	0.65981	0.03811	0.00325	0.11911	0.00249	0.00107	0.01363
6	0.29082	0.00536	0.56627	0.01444	0.00229	0.06410	0.00055	0.00074	0.00432
7	0.18648	0.00409	0.47764	0.00560	0.00170	0.03348	0.00012	0.00055	0.00132
8	0.12125	0.00321	0.39660	0.00220	0.00131	0.01707	0.00003	0.00042	0.00039
9	0.07991	0.00259	0.32458	0.00088	0.00105	0.00854	6×10^{-6}	0.00033	0.00011
10	0.05300	0.00213	0.26210	0.00036	0.00087	0.00042	1×10^{-6}	0.00027	0.00003

TABLE 4. VALUES OF VARIOUS QUANTITIES AT THE N–I PHASE TRANSITION AS PREDICTED BY THE GENERALIZED VAN DER WAALS THEORY WITH $v_{\text{att}} = -(\epsilon_0/r^6)\,\{1+\delta P_2(\cos\gamma)\}$

(P = 1 atm in all cases.)

	experimental data for	theoretical predictions for $x = 1.5$			
quantity	PAA	$\delta = 0$	$\delta = 0.01$	$\mu = 0.05$	$\delta = 0.10$
$\{\epsilon_0/(kv_0a^3)\}/10^4$ K	—	10.7	9.92	7.83	6.37
T_{NI}/K	409	408.8	408.7	408.8	408.8
$v_0\rho_{\text{nem}}$	0.62	0.559	0.547	0.506	0.468
$\Delta\rho/\rho_{\text{nem}}$	0.0035	0.0153	0.0165	0.0230	0.0347
$\Delta S/(Nk)$	0.17	1.07	1.04	1.01	1.07
η_2	0.36	0.607	0.593	0.569	0.567
η_4	0.07	0.284	0.269	0.239	0.233
τ	3.9	1.64	1.57	1.39	1.28
$(\mathrm{d}T_{\text{NI}}/\mathrm{d}P)_{P=1\,\text{atm}}/(\text{K/kbar})$	48	44	50	78	121

4. CONCLUSIONS AND FUTURE PROSPECTS

(a) *Discussion of results*

As is clear from the results presented in § 3, the van der Waals approach can yield rather good agreement with experiment if one uses an empirical mean field potential with two adjustable parameters v_0 and v_2 and one chooses a hard-core length: width ratio somewhat smaller than one might guess *a priori*. On the other hand, when one uses the generalized van der Waals theory, in which the mean field pseudo-potential $\overline{\psi}(\Omega,\rho)$ is calculated from an assumed intermolecular pair potential in a self-consistent manner, the agreement between theory and experiment is much less impressive. All of the idealizations and approximations inherent in the generalized van der Waals theory no doubt contribute to its quantitative deficiencies. In my opinion, however, in order of decreasing probable importance, the most serious defects of the theory in its present form are: (1) the neglect of short-range orientational order in the evaluation of $\overline{\psi}(\Omega,\rho)$, (2) the use of cylindrically symmetric molecular hard cores, and (3) the use of scaled particle theory to evaluate $A^*\{f(\Omega)\}$. The evidence suggesting that the use of scaled particle theory may be a significant source of error was presented in § 2. The reasons for believing that the neglect of short-range order and the use of spherocylindrical hard cores have even more serious consequences are discussed in turn below.

In §2 it was noted that all short-range translational and orientational order is neglected in the evaluation of $\overline{\Psi}(\Omega, \rho)$, except for the enforcement of the requirement that molecular hard cores not overlap. More precisely, in performing the averaging over $\boldsymbol{r}$ and Ω' in (4), it is assumed that the density of molecules with orientation Ω' at position $\boldsymbol{r}$ relative to the centre of a molecule with orientation Ω has only two values: it is equal to zero within the surface $S(\gamma)$ on which $\mathrm{e}^{-\beta v^*(\boldsymbol{r}, \gamma)}$ changes from 0 to 1; otherwise it is equal to $\rho f(\Omega')$, even for values of $\boldsymbol{r}$ just outside $S(\gamma)$. Given the success of the van der Waals theory of simple liquids, it would appear that the neglect of short-range translational order in the calculation of the mean field potential is a reasonable approximation. On the other hand, neglecting the strong short-range orientational order that no doubt exists in both nematic and isotropic phases of rod-like molecules may well have serious thermodynamic consequences. Intuitively one would expect the neglect of short-range orientational correlations when evaluating $\overline{\Psi}$ to lead to (1) an overestimate of the degree of long-range orientational order in the nematic phase (in the absence of short-range orientational order, the only way that neighbouring molecules can be strongly aligned and thus minimize their energy of interaction is for there to be very strong long-range orientational order present), (2) an energetic 'discrimination' against the isotropic phase, and (3) an exaggeration of the difference between a nematic and an isotropic phase at a given T and ρ. To obtain a rough estimate of the magnitude of these effects I have redone the van der Waals calculations for two model systems with $x = 2$ and $x = 3$ respectively, using a very crude and highly arbitrary procedure for incorporating the effects of short-range orientational order into the evaluation of $\overline{\Psi}(\Omega, \rho)$. Specifically, the procedure used when averaging $v_{\mathrm{att}}(\boldsymbol{r}, \Omega, \Omega')$ over $\boldsymbol{r}$ and Ω' was to define a spherocylindrical volume of radius $2a(1+\alpha)$ and cylindrical length l surrounding the molecule with orientation Ω and then to assume that all molecules whose centres lie within this volume also have orientation Ω. (Outside this spherocylindrical volume, the density of molecules with orientation Ω' was again assumed to be $\mathrm{e}^{-\beta v^*} \rho f(\Omega')$.) For both systems considered, α was set equal to $l/(8a)$, which means that the radius $2a(1+\alpha)$ is midway between the respective distances of closest approach of two parallel and two perpendicular hard spherocylinders of radius a and cylindrical length l. The results of these revised calculations are given in table 5, from which it is clear that the incorporation of short-range order – however crudely and arbitrarily it was done – leads to dramatically improved agreement with experiment. This argues quite strongly that the neglect of short-range orientational order in the evaluation of $\overline{\Psi}(\Omega, \rho)$ is a serious source of error in the generalized van der Waals theory.

Real nematogenic molecules clearly do not have cylindrically symmetric shapes. None the less, given the statistically free rotation about the molecular long axis in nematic liquids, it might seem that the use of spherocylindrical molecular hard cores is a reasonable approximation. However, calculations by a number of authors (Shih & Alben 1972; Straley 1974; Luckhurst *et al.* 1975), with the use of a variety of approximate theoretical approaches, suggest that the assumption of cylindrical molecular symmetry leads to significant overestimates of the degree of order in the nematic phase and of the discontinuities in ρ, H, S, η_2, etc., at the N–I transition. Most recently, for example, Gelbart & Barboy considered systems of hard ellipsoids of revolution (Gelbart & Barboy 1979) and of hard parallelepipeds (Gelbart & Barboy 1980) with principal axes of length a, b and c, constrained to lie with their longest axis parallel to one of the six axial directions of a space-fixed Cartesian coordinate system. In both instances they calculated the nematic order parameter $\eta_{2,\mathrm{NI}}$ and the relative density change $\Delta\rho/\rho_{\mathrm{nem}}$ at the N–I transition as a function of b/a with c/a held equal to 5. Both $\eta_{2,\mathrm{NI}}$ and $\Delta\rho/\rho_{\mathrm{nem}}$ were found to decrease with increasing b/a, becoming zero at $b/a = b^*/a \approx 2.3$. For $b > b^*$, the ordered phase had $\eta_2 < 0$; i.e. it was a uniaxial phase in which the shortest molecular axis was oriented parallel to the uniaxial symmetry axis. Based on these results, the authors argued that the very small values of $\Delta\rho$, ΔS, etc., observed at the N–I transition in common nematogens result from a nearly equal balance between the tendencies to form a hard-rod-like and a hard-plate-like uniaxial phase. If this is correct, then the use of cylindrically symmetric hard cores in the van der Waals theory probably makes a major contribution to the quantitative deficiences observed.

Table 5. Values of various quantities at the N–I phase transition as predicted by the generalized van der Waals theory, with and without 'correction' for the effects of short-range orientational order

(In all cases, $v_{\mathrm{att}} = -\epsilon_0/r^6$ and $P = 1$ atm.)

quantity	experimental data for PAA	theoretical predictions for $x = 3$ uncorrected	theoretical predictions for $x = 3$ 'corrected' $\alpha = 0.50$	theoretical predictions for $x = 2$ uncorrected	theoretical predictions for $x = 2$ 'corrected' $\alpha = 0.25$
$\{\epsilon_0/(kv_0a^3)\}/10^4$ K	—	7.60	10.0	7.73	12.0
T_{NI}/K	409	408.6	408.7	408.4	408.8
$v_0\rho_{\mathrm{nem}}$	0.62	0.450	0.493	0.456	0.556
$\Delta\rho/\rho_{\mathrm{nem}}$	0.0035	0.481	0.040	0.116	0.012
$\Delta S/(Nk)$	0.17	6.99	1.01	2.65	0.599
η_2	0.36	0.974	0.608	0.816	0.476
η_4	0.07	0.919	0.265	0.572	0.149
τ	4.0	1.61	7.46	1.65	3.53
$(\mathrm{d}T_{\mathrm{NI}}/\mathrm{d}P)_{P=1\,\mathrm{atm}}$/(K/kbar)	48	497	141	184	61

(b) *Suggested improvements*

Based on the discussion in the previous subsection, it appears that the most promising ways to attempt to improve the generalized van der Waals theory would be (i) to incorporate short-range orientational order into the theory in some approximate but self-consistent manner, (ii) to use molecular hard cores with lower than cylindrical symmetry, and (iii) to devise a method for evaluating the free energy functional $A^*\{f(\Omega)\}$ more accurately. Some brief comments concerning each of these suggested improvements are given in the following paragraphs.

(i) *Incorporation of short-range orientational order*

Devising a way to 'build in' short-range orientational correlations in a tractable *and* self-consistent manner is clearly a very difficult but worthwhile task. One possible way to proceed would be to replace (4) for the pseudo-potential $\bar{\psi}(\Omega,\rho)$ by

$$\bar{\psi}(\Omega,\rho) = \rho\int f(\Omega')\,\mathrm{d}\Omega'\int \mathrm{d}\boldsymbol{r}\,\mathrm{e}^{-\beta v^*(r,\gamma)}y(\boldsymbol{r},\gamma)\,v_{\mathrm{att}}(\boldsymbol{r},\Omega,\Omega'), \tag{29}$$

where $\mathrm{e}^{-\beta v^*}y$ represents some (necessarily crude) approximation to the hard-core pair correlation function $g^{(2)}(\rho,\boldsymbol{r},\Omega,\Omega')$. For the complete statistical mechanical self-consistency of the van der Waals theory to be maintained, the $y(\boldsymbol{r},\gamma)$ used could not explicitly be ρ-dependent, nor could it depend on any parameter that changes with density when $f(\Omega)$ is held constant. A reasonable functional form to use for $y(\boldsymbol{r},\gamma)$ might possibly be inferred from Monte Carlo simulations of isotropic hard-rod fluids. If no approach of this sort proves practicable, one can always fall back on some *ad hoc* method for mimicking the effects of short-range order – perhaps a somewhat more sophisticated version of the scheme described in § *a*.

(ii) *Use of non-cylindrically symmetric hard cores*

The main complication that arises if one uses molecular hard cores with lower than cylindrical symmetry in the van der Waals theory is that the evaluation of the integral

$$I(\Omega, \Omega') = \int \mathrm{d}\boldsymbol{r}\, \mathrm{e}^{-\beta v^*}\, v_{\mathrm{att}}$$

becomes much more difficult. In particular, the characterization of the surface $S(\Omega, \Omega')$ on which $\mathrm{e}^{-\beta v^*}$ changes from 0 to 1 becomes a *quite* difficult problem in solid geometry. Whether or not $I(\Omega, \Omega')$ can be evaluated in practice depends on how clever one is in choosing a hard-core shape. In my opinion, a hard ellipsoid would not be a good choice for the hard-core shape; a more promising candidate would be what can be called a capped parallelepiped, i.e. a parallelepiped with edges of lengths a, b, and l capped on the two faces of area al by a half spherocylinder of radius a and cylindrical length l and capped on the two faces of area ab by a half spherocylinder of radius a and cylindrical length b. (In this limit, $b = 0$, this becomes a spherocylinder of radius a and cylindrical length l.) The advantage of this shape is that in moving one such object about another to determine $S(\Omega, \Omega')$, one is always sliding a point on a spherocylinder or a plane over a planar or spherocylindrical surface. This leads to less complicated geometry than does sliding one ellipsoid over another. (As a trivial example of the differences encountered, note that the mutual exclusion volume of two aligned spherocylinders is a spherocylinder whereas the mutual exclusion volume of two ellipsoids is not an ellipsoid.) Based on some preliminary estimates, it seems that it *may* be possible to apply the van der Waals approach to a model system with hard cores in the shape of such a capped parallelepiped or 'stretched spherocylinder'.

(iii) *Other methods of evaluating* $A^*\{f(\Omega)\}$

In principle one could derive a more accurate hard-core free energy functional $A^*\{f(\Omega)\}$ by solving one of the common integral or integro-differential equations for the pair correlation function of the hard-core system and then evaluating $A^*\{f(\Omega)\}$ by standard statistical mechanical manipulations. In practice, however, the probability of doing this successfully for a system of hard rods seems very small at present. One must therefore look for some approximate, tractable method of evaluating $A^*\{f(\Omega)\}$ that is more accurate than scaled particle theory. Two possibilities have so far been suggested.

Savithramma & Madhusudana (1980) evaluated $A^*\{f(\Omega)\}$ for hard spherocylinders by using an extension of a method developed by Andrews (1975) for calculating the hard-sphere equation of state. In this approach the reciprocal of the thermodynamic activity, a^{-1}, is identified with the probability p that an additional hard particle can be added successfully to the system at some arbitrary point; p is then evaluated by using simple probabilistic arguments, in which the total free volume V_f in the system is written $V_f = V - N\omega(\rho)$, where $\omega(\rho)$ is determined by recourse to computer 'experiments'. Savithramma & Madhusudana expressed $\omega(\rho)$ as a seven-term power series in ρ whose coefficients were evaluated by demanding that $\omega = 2\sqrt{3}\, v_0$ at the close-packed density and that the coefficient of ρ^n ($n = 3$ to 8) in the density expansion of Pv_0/kT for an isotropic state be equal to the virial coefficient B_n determined by Monte Carlo calculation. Using

$A^*\{f(\Omega)\}$ calculated in this manner, the empirical pseudo-potential (2), and the two-term expansion of $\langle\langle|\sin\gamma|\rangle\rangle$, they determined the properties of various model systems with $x = 1.0$ to 2.90 at the N–I transition, obtaining somewhat better agreement with experiment than that produced by scaled particle theory. Given the highly approximate free volume arguments used in deriving the activity a, this improvement clearly results from 'building in' the virial equation of state for isotropic hard spherocylinders. The method is thus limited to systems for which a large number of virial coefficients are available for the isotropic hard-core system. In such cases, the 'Andrews' $A^*\{f(\Omega)\}$ could readily be used in place of the scaled particle free energy functional in the generalized van der Waals theory. I doubt, however, that this would by itself yield greatly improved results.

Another alternative to scaled particle theory that has been proposed is the y-expansion technique developed by Barboy & Gelbart (1979, 1980). In this approach, the equation of state is expanded in a power series in the variable $y = v_0\rho/(1-v_0\rho)$, i.e.

$$Pv_0/kT = \sum_{n\geqslant 1} C_n y^n, \tag{30}$$

where the coefficients C_n are related to the usual virial coefficients B_2, B_3, B_4, etc., by

$$B_{n+1} = \sum_{k=1}^{n+1} \binom{n}{k-1} C_k. \tag{31}$$

For isotropic fluids of hard particles with a variety of shapes, the y-expansion – unlike the ordinary virial expansion – has been shown to converge rapidly enough to calculate the equation of state accurately at liquid-like densities. It has been used to study the N–I phase transition in systems of hard parallelepipeds restricted to six discrete orientations (parallel to the $\pm x$, $\pm y$, $\pm z$ axes of a space-fixed Cartesian coordinate system) and to calculate the equation of state of an isotropic fluid of hard spherocylinders. (In the latter instance, truncating the expansion after the y^3 term yielded results comparable with those of scaled particle theory.) The difficulty in applying this method to nematic phases of rod-like particles allowed to adopt all orientations is that the virial coefficients B_2, B_3, B_4, etc., are generally not available and very hard to calculate. For a system of hard rods with orientational distribution function $f(\Omega)$,

$$B_n = \int\ldots\int f(\Omega_1)f(\Omega_2)\ldots f(\Omega_n)\,\beta_{n-1}(\Omega_1,\ldots,\Omega_n)\,\mathrm{d}\Omega_1\ldots\mathrm{d}\Omega_n, \tag{32}$$

where β_{n-1} is the $(n-1)$th irreducible cluster integral for n hard rods with fixed orientations $\Omega_1, \Omega_2, \ldots, \Omega_n$, respectively. $\beta_1(\Omega_1, \Omega_2)$ has been derived only for hard spherocylinders, cylinders, prolate ellipsoids and oblate ellipsoids (Onsager 1949; Isihara 1951); $\beta_2(\Omega_1, \Omega_2, \Omega_3)$ has not been derived for hard rods of any shape. Moreover, it seems highly unlikely that analytical expressions for β_2, β_3, etc., will ever be derived. As noted by Gelbart & Barboy, however, it *may* be possible to derive accurate approximate expressions for $\beta_2(\Omega_1, \Omega_2, \Omega_3)$ at least. If this proves to be so and if the y-expansion converges sufficiently rapidly in the nematic phase, this approach may turn out to be a more accurate way to evaluate $A^*\{f(\Omega)\}$. At the moment this is still an open question.

(*c*) *Extensions of the theory*

Cotter & Wacker (1978*a*) extended the van der Waals theory to nematogenic solutions, i.e. solutions that exhibit a stable nematic mesophase over some range of temperature and composition. The extended theory is applicable to mixtures of any number of components with spherocylindrical–spherical molecular hard cores. So far, however, it has been applied only to binary mixtures with effectively spherical solute molecules and rod-like solvent molecules (Cotter & Wacker 1978*b*), by using an empirical mean field pseudo-potential for the solvent molecules. (Solute and solvent molecular dimensions were estimated from tabulated van der Waals volumes, and all other energy parameters were calculated from ratios of heats of vaporization.) The temperature–mole-fraction phase diagrams calculated from the theory are in rather good agreement with experimental data (Martire *et al.* 1976) for the systems CCl_4-DHAB, $(CH_3)_4$Sn-MBBA, $(C_2H_5)_4$Sn-MBBA, $(n\text{-}C_3H_7)_4$Sn-MBBA, and $(n\text{-}C_4H_9)_4$Sn-MBBA.

More recently, Gelbart & Ben-Shaul (1982) have extended the theory to nematic mesophases subject to elastic deformations. For each of the principal elastic constants (i.e. splay, bend and twist), they derived an expansion of the form

$$k = C_{22}\eta_2^2 + C_{24}\eta_2\eta_4 + C_{44}\eta_4^2 + \ldots, \tag{33}$$

which they truncated after the term proportional to $\eta_2\eta_4$ (η_n is equal to $P_n(\cos\theta)$, as usual). These expansions were then used to investigate the dependence of the elastic constants on various molecular parameters. When experimental values are used to determine $\eta_2(T)$ and $\eta_4(T)$, the predictions of the theory are in reasonably good agreement with experimental observations.

Also quite recently, Savithramma & Madhusudana (1982*a*) have extended the van der Waals approach to systems of disc-like nematogens, using molecular hard cores in the shape of a right circular cylinder of radius a and length l and the empirical pseudo-potential (2). This model system was shown to exhibit a hard-rod-like nematic mesophase ($\eta_2 > 0$) when $x = l/2a > 1$ and a hard-disc-like nematic mesophase ($\eta_2 < 0$) when $x < 1$. Moreover, when various properties of the system at the N–I transition (e.g. $\Delta\rho/\rho_{\text{nem}}$ and $\Delta U/(NkT)$) were plotted against x, the curves were approximately symmetric about $x = 1$, suggesting that the properties of the N–I transition for disc-like nematogens are comparable in many respects with those for rod-like nematogens.

Future extensions of the van der Waals theory that would in my opinion be particularly desirable include (1) extending the theory to allow for the possibility of smectic as well as nematic ordering, and (2) modifying the theory to take into account the flexibility of the molecular 'end chains' of real nematogens or smectogens. As a preliminary endeavour before attempting either of these extensions, a student of mine, L. Petrone, is working at present on a lattice version of the van der Waals theory that incorporates end-chain flexibility in a fairly realistic manner and can treat smectic ordering.

(*d*) *Concluding remarks*

In conclusion, I should like to return to a point emphasized in the introduction, namely that the van der Waals theory is intended to be a 'chemist's' theory to be used to study the relation between molecular structure and mesomorphic behaviour. In my opinion there are two main requirements that a successful theory of this sort must meet: (i) although quantitative agreement between theory and experiment is certainly not required, the agreement must be good enough so that one can believe qualitative trends and explanations suggested by the theory – even rather subtle ones; (ii) it must be possible to relate the parameters of the model system to the molecular size, shape, polarity, polarizability, etc., of a particular mesogen in some reasonably straightforward manner. The van der Waals approach with the empirical pseudo-potential (2) satisfies requirement (i) nicely, but falls far short of meeting requirement (ii) because there is no clear way to relate the value of the parameter v_2 to the characteristics of a particular molecule. On the other hand, the generalized van der Waals theory in its present state has some trouble with requirement (i) owing to its severe overestimate of the orientation dependence of the mean field potential. This latter problem can, however, clearly be corrected. (The only question is whether it can be corrected in a less crude and arbitrary manner than that described in §*a*.) Furthermore, although the generalized van der Waals approach does not completely satisfy requirement (ii) at present, it comes closer, in my opinion, than any other molecular theory proposed to date. In short, although much remains to be done, a start has clearly been made toward the goal of developing a successful 'chemical' theory of thermotropic mesomorphism. Modifying the van der Waals theory to take into account molecular flexibility, non-cylindrically symmetric molecular shapes, and the existence of smectic order would clearly all be large steps toward this goal.

REFERENCES

Andrews, F. C. 1975 *J. chem. Phys.* **62**, 272–275.
Barboy, B. & Gelbart, W. M. 1979 *J. chem. Phys.* **71**, 3053–3062.
Barboy, B. & Gelbart, W. M. 1980 *J. statist. Phys.* **22**, 709–742.
Baron, B. A. & Gelbart, W. M. 1977 *J. chem. Phys.* **67**, 5795–5801.
Cotter, M. A. 1974 *Phys. Rev.* A **10**, 625–636.
Cotter, M. A. 1977*a* *J. chem. Phys.* **66**, 1098–1106.
Cotter, M. A. 1977*b* *J. chem. Phys.* **66**, 4710–4711.
Cotter, M. A. 1977*c* *J. chem. Phys.* **67**, 4268–4270.
Cotter, M. A. 1979*a* In *The molecular physics of liquid crystals* (ed. G. R. Luckhurst & G. W. Gray), pp. 169–180. London: Academic Press.
Cotter, M. A. 1979*b* In *The molecular physics of liquid crystals* (ed. G. R. Luckhurst & G. W. Gray), pp. 181–189 London: Academic Press.
Cotter, M. A. & Martire, D. E. 1970*a* *J. chem. Phys.* **52**, 1909–1919.
Cotter, M. A. & Martire, D. E. 1970*b* *J. chem. Phys.* **53**, 4500–4511.
Cotter, M. A. & Wacker, D. C. 1978*a* *Phys. Rev.* A **18**, 2669–2675.
Cotter, M. A. & Wacker, D. C. 1978*b* *Phys. Rev.* A **18**, 2676–2682.
Gelbart, W. M. & Baron, B. A. 1977 *J. chem. Phys.* **66**, 207–213.
Gelbart, W. M. & Barboy, B. 1979 *Molec. Cryst. liq. Cryst.* **55**, 209–226.
Gelbart, W. M. & Barboy, B. 1980 *Acct. chem. Res.* **13**, 290–296.
Gelbart, W. M. & Ben-Shaul, A. 1982 *J. chem. Phys.* **77**, 916–933.
Gelbart, W. M. & Gelbart, A. 1977 *Molec. Phys.* **33**, 1387–1398.
Isihara, A. J. 1951 *J. chem. Phys.* **19**, 1142–1147.
Lasher, G. 1970 *J. chem. Phys.* **53**, 4141–4146.
Longuet-Higgins, H. C. & Widom, B. 1964 *Molec. Phys.* **8**, 549–556.
Luckhurst, G. R. 1979 In *The molecular physics of liquid crystals* (ed. G. R. Luckhurst and G. W. Gray), pp. 85–119. London: Academic Press.
Luckhurst, G. R., Zannoni, C., Nordiv, P. L. & Segre, U. 1975 *Molec. Phys.* **30**, 1345–1351.
Maier, W. & Saupe, A. 1959 *Z. Naturf.* **14**a, 882–889.
Maier, W. & Saupe, A. 1960 *Z. Naturf.* **15**a, 287–292.
Martire, D. E., Oweimreen, G. A., Ågren, G. I., Ryan, S. G. & Peterson, H. T. 1976 *J. chem. Phys.* **64**, 1456–1464.
McColl, J. R. & Shih, C. S. 1972 *Phys. Rev. Lett.* **29**, 85–87.
Monson, P. A. & Rigby, M. 1978 *Molec. Phys.* **35**, 1337–1342.
Onsager, L. 1949 *Ann. N.Y. Acad. Sci.* **51**, 627–643.
Reiss, H., Frisch, H. L. & Lebowitz, J. L. 1959 *J. chem. Phys.* **31**, 369–380.
Savithramma, K. L. & Madhusudana, N. V. 1980 *Molec. Cryst. liq. Cryst.* **62**, 63–80.
Savithramma, K. L. & Madhusudana, N. V. 1982*a* *Molec. Cryst. liq. Cryst.* (In the press.)
Savithramma, K. L. & Madhusudana, N. V. 1982*b* *Molec. Cryst. liq. Cryst.* (In the press.)
Shih, C. S. & Alben, R. 1972 *J. chem. Phys.* **57**, 3055–3061.
Straley, J. P. 1974 *Phys. Rev.* A **10**, 1881–1887.
Timling, K. 1974 *J. chem. Phys.* **61**, 465–469.
Vieillard-Baron, J. 1974 *Molec. Phys.* **28**, 809–818.

Discussion

J. D. Litster (*M.I.T., Cambridge, Massachusetts, U.S.A.*) I have two questions.

(1) How much better is Professor Cotter's approach than the simple Maier–Saupe model?

(2) Can Professor Cotter estimate the difference between the first order transition temperature and the extrapolated second order transition from short range order measurements in the isotropic phase?

Martha A. Cotter.

(1) If one uses the van der Waals approach with an empirical mean-field potential and treats the hard-core length: width ratio and the energy parameters v_0 and v_2 as adjustable parameters, one obtains agreement with experiment comparable with that obtained from the simple Maier–Saupe theory – better agreement in some respects, worse in others. I do not think this is of great significance, however. As I have tried to indicate, what I think the van der Waals theory is better for is studying the relation between molecular structure and mesophase stability and properties. On the other hand, the van der Waals approach is no doubt worse than the simple Maier–Saupe approach for studying the N–I phase transition *per se* (i.e. in the context of the modern theory of phase transitions) because the former exaggerates the strength of the first-order N–I transition even more than the latter.

(2) One can no doubt calculate $T_c - T^*$ from the van der Waals theory, although I have not done so. Since the theory does not consider short-range orientational order in the isotropic phase and greatly overestimates the strength of the N–I transition, I suspect that it will also greatly overestimate $T_c - T^*$.

Lin Lei (*Institute of Physics, Chinese Academy of Sciences, Beijing, China*). We have recently extended the Landau–de Gennes theory to treat the pressure effects of nematics. Now,

$$G(T,P) = G_0(T,P) + \tfrac{1}{2}a\{T - T^*(P)\}S^2 - \tfrac{1}{3}B(P)S^3 + \tfrac{1}{4}C(P)S^4.$$

For PAA (B, C independent of P), our theory is able to explain all the existing pressure experiments (not too close to the N–A transition). Above $P = 472$ MPa and $258 < T < 251$ °C, a re-entrant isotropic phase is predicted to exist (Lin Lei & Liu Jiagang, *Kexue Tongbao* **27**, 784 (1982); *Molec. Cryst. liq. Cryst.* (in the press)). It will be very interesting to check this result with molecular calculations. Since Professor Cotter's van der Waals theory is simple and tractable, relatively speaking, I wonder if it can be used to calculate the $T_{NI}(P)$ curve at high pressure (*ca.* 472 MPa)? If so, has this been done yet?

Martha A. Cotter. I have not calculated the N–I transition temperature at high pressures from the generalized van der Waals theory, although it can readily be done. However, Savithramma & Madhusudana (*Molec. Cryst. liq. Cryst.* (in the press)) have calculated $T_{NI}(P)$ for pressures up to 600 MPa, using the van der Waals approach with an empirical mean-field potential. They did not observe a re-entrant isotropic phase.