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On the conformational effects of intermolecular interactions in nematics

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A perturbation expansion of the pair correlation function is used to derive the molecular field self-consistency equations for non-rigid molecules. The order parameters and the thermodynamic functions are expressed directly in terms of the segmental interaction coupling constants. The values of these constants for the 4-*n*-alkyl-4′-cyanobiphenyls (NCB) are determined by analysing the orientational order parameters observed by N.M.R. in the nematic phase; they are in reasonable agreement with values obtained from calculations of the nematic–isotropic transition temperatures. It is found that contributions of the isotropic intermolecular interactions to the conformational energy of the alkyl chain are comparable in magnitude to the direct intramolecular contributions.

1. Introduction

Whilst anisotropy of molecular shape is the microscopic basis of liquid-crystalline behaviour, molecular flexibility is a determining factor of stability of a given mesophase relative to the solid and the isotropic liquid as well as relative to other possible mesophases. The effects of flexibility are reflected rather directly on the segmental orientational order profile of the molecule. Accordingly, theoretical developments on conformational statistics of liquid crystal molecules [1–9] are to a large extent directed towards the interpretation of the results of experimental studies of orientational order and of the phase transition thermodynamics.

By realizing the importance of correlations between the orientational motion of the molecule and its conformational state, Emsley *et al.* [6] developed a simple theory for the interpretation of N.M.R. spectra of the deuteriated alkyl chain in the nematic phase. The theory is based on a single molecule, effective potential conforming to the following assumptions. (*a*) The anisotropic part of the molecular energy is the sum of the orientational energies of the individual segments. (*b*) These energies are given by a truncated expansion in spherical harmonics of the segmental orientations. Chain segments of the same type (C–C or C–H bonds) have identical, conformationally independent expansion coefficients, irrespective of their position within the chain. (*c*) The isotropic part of the potential is given by the conformational energy of the non-interacting chain. The same form of potential was used by Marcelja [5] in his early mean field study of the effects of chain length on nematic order.

The resulting singlet probability distribution exhibits direct orientation–conformation correlations and provides a good description of the essential features of end-chain orientational order. However, the values of the conformational energy parameters required to reproduce [6, 10, 11] the results of N.M.R. measurements show considerable variation with chain length and in some cases exceed the range of acceptable values for gaseous and liquid alkanes. This situation seems to be typical of a variety of calculations [4, 9, 12] where the free chain energy states are used to describe the conformational statistics in the mesophase.

Such discrepancies are attributable to possible oversimplifications introduced by the basic assumptions (*a*), (*b*) and (*c*). There is, in fact, no *a priori* justification for ignoring multisegment interaction terms, or dependences of the segmental interaction coefficients on position and conformation, nor for excluding isotropic (conformational) energy contributions resulting from intermolecular interactions. But on the other hand, considerations restricted to the singlet probability do not offer a way of generalizing the effective potential in any of these respects (without introducing *ad hoc* phenomenological energy terms or constraints).

The present work is addressed to the study of these assumptions, and related generalizations, from the point of view of their implications on the intermolecular interaction. In the next section a relation between the singlet distribution and the effective intermolecular interaction potential is established in the context of a perturbation expansion of the long range part of the pair correlation function. A self-consistent mean field approximation suitable for the description of non-rigid molecules is derived as the first order solution. Section 3 contains a detailed account of the assumptions leading to the effective potential of the simplest form and of their implications on the intermolecular interactions in the mean field approximation. The basic parameters of the interaction are then determined by simulating the segmental orientational order parameters for the 4-*n*-alkyl-4′-cyanobiphenyls (NCB) in the nematic phase and are subsequently used to calculate the temperature, the entropy differences and the order parameter values at the nematic–isotropic phase transition. Section 4 describes the contributions of the intermolecular interactions to the conformational energy. A calculation performed by properly taking into account the spatial extension of the flexible chain when evaluating the isotropic part of the intermolecular segmental interaction shows that it is possible to reproduce the observed orientational order using the free chain conformational energy parameters.

2. Derivation of the self-consistent molecular field approximation for non-rigid molecules

The symmetries of liquid crystals and many of their readily measurable properties are directly reflected on the structure of the single molecule distribution function $P_1(x)$, which therefore is the natural starting point of mesophase statistical mechanical theories. The effective molecular potential $V_1(x)$ is defined in terms of $P_1(x)$ by

$$P_1(x) = (1/Z_1)\exp(-V_1(x)/kT), \qquad (1)$$

where x represents collectively all the relevant variables (positional, orientational, conformational), and Z_1 is the usual normalization factor. $V_1(x)$ may be decomposed into a part E_0 describing the direct intramolecular interaction, hence depending only on the conformational state of the molecule, and a part V produced by intermolecular interactions,

$$V_1(x) = E_0(n) + V(x), \qquad (2)$$

where n stands for the purely conformational subset of the variables x. It is possible to express $V(x)$ to any desired accuracy by retaining a sufficient number of terms in an expansion of the form

$$V(x) = \sum_q v_q f(x;\, q), \tag{3}$$

where $f(x;\, q)$ are appropriate basis functions labelled by the collective index q. The effects of intermolecular interactions are then contained entirely in the expansion coefficients v_q. Although a relatively small number of these coefficients are normally sufficient to account for the observed properties, they cannot be considered as the fundamental quantities of a theory. Rather, a theory is considered to be complete at the level of single molecule statistics if it describes the dependence of the v_qs on temperature and molecular characteristics.

A formal procedure towards this end would start by relating the v_qs to the effective intermolecular potential $U(x, x')$ through the condition

$$P_1(x) = \int P_2(x, x')\, dx'. \tag{4}$$

Here $P_2(x, x')$ is the pair probability distribution function, defined in terms of $U(x, x')$ according to

$$P_2(x, x') = (1/Z_2) \exp \{-(E_0(n) + E_0(n') + U(x, x'))/kT\}. \tag{5}$$

The procedure can in principle be continued by relating $U(x, x')$ to the three molecule effective potential etc., but here we shall restrict our consideration to the first step. The mathematical problem involved in this step is to use the condition of equation (4) in order to determine the form of $U(x, x')$ that would be compatible with a given truncated form of $V(x)$. The respective solutions are not unique in general, nor is it possible to obtain them exactly. To provide the framework for a suitable approximation scheme, we introduce the pair correlation function

$$g(x, x') = P_2(x, x')/P_1(x)P_1(x') \tag{6}$$

and the associated correlation potential

$$W(x, x') = -kT \log(g(x, x')). \tag{7}$$

According to equation (4) g satisfies the condition

$$\langle g(x, x')\rangle_x = \int P_1(x) g(x, x')\, dx = 1. \tag{8}$$

The correlation function can always be factorized into a part g_0 which prevents overlap of two molecules and a part g_L which describes all correlations in excess of mutual excluded volume effects. The g_0 part is supposed to be known once the geometry of each conformation and the type of intermolecular repulsion (hard-core, r^{-12}, etc.) are specified. More generally, the factorization

$$g(x, x') = g_0(x, x') g_L(x, x') \tag{9}$$

can be understood as a decomposition of the correlation potential into a known part W_0 that includes the short distance repulsion, and a softer part W_L representing longer ranged contributions, i.e.

$$W(x, x') = W_0(x, x') + W_L(x, x'), \tag{10}$$

with the potentials W_0, W_L defined in terms of g_0, g_L by analogy to equation (7). In view of these definitions equations (5) and (8) are written

$$U(x, x') = V(x) + V(x') + W_0(x, x') + W_L(x, x') + kT\log(Z_1^2/Z_2). \tag{5'}$$

and

$$\langle \exp(-W_L(x, x')/kT) \rangle_{x[x']} = 1/\langle g_0(x, x') \rangle_x, \tag{8'}$$

where use has been made of the notation

$$\langle F(x, x') \rangle_{x[x']} = \langle g_0(x, x') F(x, x') \rangle_x / \langle g_0(x, x') \rangle_x.$$

This procedure transforms the problem of expressing a given set of v_qs in terms of $U(x, x')$ into that of determining W_L subject to the condition of equation (8′). This transformation offers a way of obtaining approximation solutions by truncating the expansion

$$\langle \exp(-W_L/kT) \rangle = \exp(-\langle W_L/kT \rangle + (\langle (W_L/kT)^2 \rangle - \langle W_L/kT \rangle^2)/2 + \dots). \tag{11}$$

Assuming that a truncation at the first term is meaningful, we obtain, in the resulting linear approximation, the expression

$$\langle W_L(x, x') \rangle_{x[x']} = kT\log(\langle g_0(x, x') \rangle_x) \tag{12}$$

for equation (8′), and by averaging both sides of equation (5′) we find the desired relation between U and V,

$$\langle U(x, x') - W_0(x, x') \rangle_{x[x']} = V(x') + \langle V(x) \rangle_{x[x']} + kT\log(\langle g_0 \rangle_x Z_1^2/Z_2). \tag{13}$$

Provided that $g_0(x, x')$ is equal to 1 everyhwere except in a region of the size of a few molecular diameters, the positional integration associated with the averaging operations in equations (12) and (13), when performed over the macroscopic volume of the sample V_s, will yield

$$\langle g_0(x, x') \rangle_x = 1$$

and

$$\langle V(x) \rangle_{x[x']} = \langle V(x) \rangle_x = \text{constant},$$

to within terms that vanish as $\{V_{\text{molecule}}/V_s\}$. Hence these equations may be rewritten as

$$\langle W_L(x, x') \rangle_{x[x']} = 0 \tag{12'}$$

and

$$\langle u(x, x') \rangle_{x[x']} = V(x) + \text{constant}, \tag{13'}$$

where

$$u(x, x') = U(x, x') - W_0(x, x'),$$

and the additive constant is of no significance since the potentials V and U are defined in equations (1) and (5) to within arbitrary additive constants.

The linear approximation equations exhibit the trivial solution

$$W(x, x') = 0,$$

which is also a solution of the exact equations (5′) and (8′), and corresponds to

$$u(x, x') = V(x) + V(x'),$$

i.e. as in the case of non-interacting molecules in an external field. They also allow for possible mean field type solutions with

$$W(x, x') \neq 0,$$

in which case equation (13) represents the self-consistency conditions on the mean field $V(x)$.

It should be noted that equation (12) and (13) give a very general form of the self-consistent molecular field approximation since no specific assumptions are made about the detailed structure of g_0, U and V, nor is any distinction made between conformational, positional or orientational variables in deriving these equations. The only essential assumption is that the decomposition of $W(x, x')$ in equation (10) is such that a sensible truncation of the expansion of equation (11) at the linear term is possible. If x is restricted to positional and orientational variables then equation (12) reproduces the familiar mean field equations for rigid molecules as derived by different procedures [13–15].

3. Nematic order and conformational statistics of the alkyl chain

The flexible molecules are assumed to consist of a number of uniaxial segments of fixed lengths. The orientation of the ith segment relative to the macroscopic frame is described by a unit vector $\mathbf{w}_i$ pointing along the direction of the principal axis of the segmental interaction tensor. The orientational state of the entire molecule is then completely specified given the orientations $\mathbf{w}_i$ of its segments or, equivalently, given the orientation $\mathbf{w}$ of the molecular frame (attached to a particular segment) and the set of orientations of all the segments relative to that frame. The latter set is denoted by the collective conformational index n. The position $\mathbf{R}$ of the molecule may be represented by the position of a particular segment, or of the centre of mass, or of a properly defined centre of interaction.

We shall consider apolar nematic phases where, as a result of translational invariance, we may write

$$P_1(x) = p_1(\mathbf{w}, n)/V_s,$$

$$V(x) = V(\mathbf{w}, n)$$

and

$$u(x, x') = u(\mathbf{R} - \mathbf{R}'; \mathbf{w}, n, \mathbf{w}', n').$$

The apolarity of the phase implies that these functions are symmetric with respect to the exchange of $\mathbf{w}$ with $-\mathbf{w}$. Under these conditions the expansion of equation (3) can be truncated at the second rank spherical harmonic terms to give the simplest non-trivial form of the effective potential,

$$V(\mathbf{w}, n) = v_0 + \sum_i v_2^i Y(\mathbf{w}_i \cdot \mathbf{N}), \tag{14}$$

where $\mathbf{N}$ is the nematic principal axis and

$$Y(\mathbf{w}_i \cdot \mathbf{N}) = (3(\mathbf{w}_i \cdot \mathbf{N})^2 - 1)/2.$$

With v_0 and v_2^i chosen as constants, the property of additivity of segmental energies in equation (14) is a result of neglecting anisotropic multi-segment contributions of the form $Y(\mathbf{w}_i \cdot \mathbf{N})Y(\mathbf{w}_j \cdot \mathbf{N}) \ldots$.

In order to use equation (13′) to determine the form of $u(x, x')$ implied by the hypothesis of conformational independence of v_0 and v_2^i it is necessary to specify $g_0(x, x')$. Clearly, from a computational point of view, the most simplifying way of preventing molecular overlap is to take g_0 to depend only on the intermolecular distance $r = |\mathbf{R} - \mathbf{R}'|$. This amounts to approximating the conformational dependent, and geometrically rather complicated, mutual excluded volume by an effective sphere of radius R_0. Using $g_0(x, x') \approx g_0(r)$ in equation (13′) it follows that the form of the intermolecular potential compatible with equation (14) is

$$u(r; \mathbf{w}, n, \mathbf{w}', n') = \sum_{ii'} \{u_0^{ii'}(r) + u_2^{ii'}(r) Y(\mathbf{w}_i \cdot \mathbf{w}_{i'})\}, \tag{15}$$

with the coefficients v_2^i subject to the self-consistency conditions

$$v_2^i = \sum_{i'} \bar{u}_2^{ii'} \langle Y(\mathbf{w}_i \cdot \mathbf{N})\rangle, \tag{16}$$

where

$$\bar{u}_2^{ii'} = \int u_2^{ii'}(r) g_0(r)\, dr/V_s, \tag{17}$$

and the angular brackets imply averaging over $\mathbf{w}'$, n' with the distribution $p_1(\mathbf{w}', n')$. Equation (16) relates the expansion coefficients of the single molecule potential to the effective coupling constants $\bar{u}_2^{ii'}$ which are the fundamental quantities of the theory at this level. In view of equations (1), (2) and (16) the singlet distribution is completely determined by specifying these quantities and the intramolecular coupling constants describing the free molecule conformational energy, $E_0(n)$.

To formulate a definite model we consider a molecule consisting of a rigid uniaxial core and a flexible alkyl chain, and make the following assumptions regarding the details of the interaction.

(i) The intermolecular interaction of the chain is a result of the uniaxial interactions of its individual C–C bonds. The unit vectors, $\mathbf{w}_i$, associated with the chain segments coincide with the respective C–C bond directions. There are just three independent intermolecular coupling constants corresponding to core–core, bond–bond and core–bond interactions. The number of independent constants is further reduced by assuming factorizability of the couplings according to

$$\bar{u}_2^{ii'} = -\bar{u}_2 h^i h^{i'}. \tag{18}$$

In this case we may take $h^i = 1$ when i refers to the core, and $h^i = h$ for any C–C bond of the chain. The intermolecular interactions are then completely specified by the two parameters $\bar{u}_2$ and h. Factorizability is theoretically exact when the molecules interact via dispersion forces.

(ii) The intramolecular C–C bond interactions are described in the rotational isomeric state approximation [16]. Only interactions between second and third nearest neighbours are included. In the standard three state approximation the respective coupling constants are the gauche energy E_g and the energy of the $g^{\mp}g^{\pm}$ sequences, $E_{g^{\mp}g^{\pm}}$. A tetrahedral geometry is assumed for all the C–C and C–H bonds of the chain. Intramolecular interactions between chain segments and the core are ignored.

These assumptions are not essential to the theory. They are usually made [5, 9, 10, 11] in order to simplify the calculations but can be relaxed in various ways to enrich the structure of the interactions if necessary. Nevertheless, the simplifying effect of the factorizability assumption on equation (18) is noteworthy since it leads to a single self-consistency condition. In particular, by defining the molecular function

$$S(\mathbf{w}, n) = \sum_i h^i Y(\mathbf{w}_i \cdot \mathbf{N}), \tag{19}$$

the singlet distribution is written as

$$P_1(\mathbf{w}, n) = (1/z)\exp(bS(\mathbf{w}, n)\langle S\rangle + e_0(n)), \tag{20}$$

where $b = \bar{u}_2/kT$, $e_0(n) = -E_0(n)/kT$ and the normalization factor is

$$z = \int \exp(bS(\mathbf{w}, n)\langle S\rangle + e_0(n))\, d\mathbf{w}dn. \tag{21}$$

In view of equation (18) and (20), the conditions of equation (16) reduce to a self-consistency condition on the generalized order parameter $\langle S\rangle$ of the flexible molecules,

$$\langle S\rangle = (1/z)\int S(\mathbf{w}, n)\exp(bS(\mathbf{w}, n)\langle S\rangle + e_0(n))\, d\mathbf{w}dn \tag{22}$$

and a constant ratio relation

$$v_2^{\text{bond}}/v_2^{\text{core}} = h. \tag{23}$$

To express the thermodynamic quantities in this approximation we determine the dependence of the partition function Q on $\langle S\rangle$ by requiring that, for fixed T and V_s, the equilibrium value of $\langle S\rangle$ corresponds to a minimum of the Helmholtz free energy

$$A = -kT\log(Q).$$

Thus by writing $Q = zL$, where L is a function of $\langle S\rangle$ determined so as to give

$$dA/d\langle S\rangle = 0,$$

and using the alternative form of equation (22), namely

$$d\log(z)/d\langle S\rangle = b\langle S\rangle, \tag{24}$$

we find the free energy

$$A = \{b\langle S\rangle^2/2 - \log(z)\}kT + A_0, \tag{25}$$

where A_0 is independent of $\langle S\rangle$. The free energy in the isotropic phase is obtained by setting $\langle S\rangle = 0$ in equations (25) and (21). As a result of the appearance of a single order parameter, equations (22) and (25) bear a formal resemblance to the corresponding equations of the Maier–Saupe theory. Similar expressions were used in the mean field theory of Marcelja, where, however, the core and chain orientational order are decoupled in the self-consistency equations [5, 10].

The constant ratio condition of equation (23) is a measure of the validity of the factorizability assumption and is supported by the results of N.M.R. temperature dependent studies [10, 11]. Following a different approach, Luckhurst [15] derived the constant ratio condition by treating the nematic phase as a mixture of rigid cores and chain segments.

Table 1. Results of fits to N.M.R. measurements of orientational order in the nematic phase of NCBs and of mean field predictions for the nematic–isotropic phase transition. The non-interacting chain conformational states are used, with E_g treated as a fitting parameter and $E_{g\mp g\pm} = 0$. The experimental values [21] of $\langle Y_{\mathrm{core}} \rangle_{\mathrm{NI}}$ are written in parentheses next to the respective predictions. Phase transition results are obtained using $h = 0{\cdot}32$ for all compounds.

N	5	6	7	8
E_g/kJ mol^{-1}	1·9 (±0·6)	2·7 (±0·3)	2·1 (±0·6)	3·5 (±0·3)
$\bar{u}_2$/kJ mol^{-1}	5·4 (±0·5)	5·4 (±0·3)	5·3 (±0·3)	4·8 (±0·3)
h	0·34 (±0·07)	0·30 (±0·05)	0·36 (±0·08)	0·35 (±0·06)
$(\bar{u}_2)_{\mathrm{NI}}$/kJ mol^{-1}	5·9	5·5	5·6	4·8
$\langle Y_{\mathrm{core}} \rangle_{\mathrm{NI}}$	0·49 (0·3)	0·40 (0·27)	0.52 (0·33)	0·40 (0·31)
$\langle S^* \rangle_{\mathrm{NI}}$	0·39	0·31	0·38	0·29
Ds_{NI}/J mol^{-1} K^{-1}	4·3	2·9	5·1	2·6

To test the predictions that follow from equation (14), the singlet distribution of equation (20) was used to determine the values of the interaction parameters $\bar{u}_2$ and h by fitting deuterium N.M.R. data covering the entire nematic range of 5CB and 8CB [12, 17] and also carbon-13 N.M.R. data on 5CB, 6CB and 7CB [18]. In these calculations the C–C bond linking the cyanobiphenyl group to the alkyl chain is counted as part of the rigid core and defines the direction of the core principal axis. The simulation was performed by treating E_g, $\bar{u}_2$ and h as fitting parameters. The results are summarised in table 1.

The alkyl chain order parameters were reproduced with an average accuracy varying from about 12 per cent for 5CB to 3 per cent for 8CB. Although the details of the predicted profiles depend on the relative weights attributed directly or indirectly to the experimental points (minimization of absolute or relative overall deviation, constraints on maximum acceptable individual deviations, inclusion of experimental errors, etc.), the methyl group predictions are generally the least accurate as is the case with calculations involving just core and (equivalent) C–C bond interactions [10]. It is found that the overall accuracy tends to improve with increasing chain length and temperature. The ranges of variation of E_g, $\bar{u}_2$ and h that produce an increase of 3 per cent in the average percentage deviation are indicated next to the calculated values of these quantities in order to provide a measure of the sensitivity of the fit. The odd-N compounds appear to be relatively insensitive to variations of E_g.

The $\bar{u}_2$ values exhibit a slow but systematic tendency to decrease with increasing N. There is also a slight temperature dependence of $\bar{u}_2$ and h. However, their overall variations with chain length and temperature do not exceed 30 per cent and thus in a first approximation it is reasonable to consider them as temperature independent and their average values as representative of the entire homologous series. In any case, such variations are to some extent expected as a result of the implicit dependence of these quantities on the effective molecular radius R_0, according to equation (17).

The basic difficulty is associated with the wide variations of the calculated E_g values with N. These variations cover almost the entire range of E_g values reported in the literature for gaseous and liquid alkanes [16, 19]. The calculated values of E_g for even-N members are notably above the result of recent measurements [19] of E_g in alkanes (~ 2 kJ mol^{-1}). The calculation is not sensitive to reasonable (50 per cent) variations of $E_{g\mp g\pm}$ about its free chain value (~ 12 kJ mol^{-1}). However, much more accurate fits are obtained with $E_{g\mp g\pm} = 0$, indicating a suppression of third neighbour interactions.

The nematic–isotropic phase transition predictions are based on the expression of equation (25) for the free energy and the assumption that $\bar{u}_2$, h, E_g and $E_{g\mp g\pm}$ are temperature independent. The values of E_g as determined from the N.M.R. fits were used, together with an average value of h equal to 0·32, to determine the phase transition values of the reduced temperature b_{NI}, the entropy difference Ds_{NI}, the core order parameter $\langle Y_{\mathrm{core}}\rangle_{\mathrm{NI}}$ and the molecular order parameter $\langle S^*\rangle_{\mathrm{NI}}$. The latter is a form of $\langle S\rangle$ normalized to 1 at perfect alignment, i.e. $\langle S^*\rangle = \langle S\rangle/(\langle S\rangle_{T\to 0})$, and gives a suitable measure of the overall orientational order of the flexible molecule.

The intermolecular coupling constant values, as determined from the phase transition calculation, namely

$$(\bar{u}_2)_{\mathrm{NI}} = kT_{\mathrm{NI}}b_{\mathrm{NI}}, \tag{26}$$

where T_{NI} is the measured phase transition temperature [20], are in reasonable agreement with the values obtained from the orientational order simulation. Also the even–odd effect is well reproduced by the calculated values of $\langle Y_{\mathrm{core}}\rangle_{\mathrm{NI}}$, $\langle S^*\rangle_{\mathrm{NI}}$ and Ds_{NI}. In view, however, of the underlying mean field approximation and the discrepancies associated with the conformational energy parameters, the numerical predictions should be understood as rough estimates of these quantities.

The values of h, E_g and $E_{g\mp g\pm}$ found for 5CB and 8CB and also the $\langle Y_{\mathrm{core}}\rangle_{\mathrm{NI}}$ predictions are in agreement with results of analogous calculations [6, 10, 21] based essentially on equations (14) and (23).

4. Conformational contributions of intermolecular interactions

The results of the preceding section, without providing direct indications of any severe failure of the assumptions about the additivity and the factorizability properties of the interaction, suggest, through the inadequacy of the free chain energy alone to account for the observed order, that the conformational dependence of the isotropic part v_0 in equation (14) is not negligible. In terms of the effective intermolecular potential of equation (15) this means that the spatial extension of the molecules ought to be taken into account by evaluating the interaction energy of each pair of segments at the respective intersegmental distance instead of using a common intermolecular distance r for all pairs.

Accordingly we consider, in the context of additivity and factorizability, the following expression for the intermolecular potential,

$$u(r;\, \mathbf{w}, n, \mathbf{w}', n') = -\sum_{ii'} h^i h^{i'}\{u_0(|\mathbf{R}_i - \mathbf{R}_{i'}|) + u_2(|\mathbf{R}_i - \mathbf{R}_{i'}|)\,Y(\mathbf{w}_i\cdot\mathbf{w}_{i'})\}, \tag{27}$$

where $\mathbf{R}_i$ denotes the position of the ith segment. To perform the positional integration implied in equation (13′) it is convenient to use the segmental positions $\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}$ relative to the molecular frame and to identify $\mathbf{R}$ with the position of the molecular centre of interaction defined by the condition

$$\sum_i h^i\mathbf{r}_i = 0. \tag{28}$$

Obviously each conformation has its own set of segmental positions $\mathbf{r}_i$ and centre of interaction.

In the spherical approximation to g_0, the result of the positional averaging can be expressed in the form of a series expansion,

$$\begin{aligned}\bar{u}_0(i, i') &= \int u_0(|\mathbf{r} + \mathbf{r}_i - \mathbf{r}_{i'}|)g_0(r)\,dr/V_s \\ &= \bar{u}_0^{(0)} + \bar{u}_0^{(1)}(\mathbf{r}_i - \mathbf{r}_{i'})^2 + \bar{u}_0^{(2)}\{(\mathbf{r}_i - \mathbf{r}_{i'})^2\}^2 + \dots, \end{aligned} \tag{29}$$

and similarly for $\bar{u}_2(i, i')$. The $\bar{u}_0^{(0)}$ term is trivial. In contrast, the $\bar{u}_2^{(0)}$ term is supposed to represent the leading contribution to the anisotropic interaction. Higher order $\bar{u}_2^{(m)}$ terms introduce conformational and positional dependence of the segmental orientational energy and also higher than second rank anisotropies. Hence an approximation where only the leading terms are retained corresponds to

$$\bar{u}_0(i, i') \approx \bar{u}_0^{(1)}(\mathbf{r}_i - \mathbf{r}_{i'})^2, \quad \bar{u}_2(i, i') \approx \bar{u}_2^{(0)} = \bar{u}_2. \tag{30}$$

It should be noted that equation (29) is essentially an expansion in powers of the parameter $|\mathbf{r}_i - \mathbf{r}_{i'}|/2R_0$ and is therefore expected to be less accurate for the outer segments where r_i is comparable to the effective radius R_0. However, with g_0 treated in the spherical approximation, it is questionable whether the inclusion of higher order terms, or an exact integration in equation (29), constitute real improvements. According to equations (13′) and (28) the isotropic part of $V(\mathbf{w}, n)$ in the approximation of equation (30) is given by

$$v_0(n) = \bar{u}_0^{(1)}\left(\sum_{i'} h^{i'}\right)\left(\sum_i h^i r_i^2\right), \tag{31}$$

and exhibits direct dependence on chain length and segment position. Following equations (2) and (30), the leading corrections to the conformational energy are taken into account simply by using

$$E(n) = E_0(n) + v_0(n)$$

in place of $E_0(n)$ in the singlet distribution of equation (20).

Results obtained with $E(n)$ are shown in table 2. In this calculation E_g was no longer an adjustable parameter. The quantities $\bar{u}_2$, h and $E_0^{(1)} = \bar{u}_0^{(1)}d^2$, where d denotes the length of the C–C bonds of the chain, were determined by fitting the N.M.R. data with $E_g = 2\,\mathrm{kJ\,mol^{-1}}$ for all compounds. The centre of interaction of each molecular conformation was specified according to equation (28), with the positions of the chain segments represented by the C–C bond midpoints and that of

Table 2. Results of fits to N.M.R. measurements of orientational order in the nematic phase of NCBs and of mean field predictions on the nematic–isotropic phase transition obtained by including the leading contributions of the isotropic interactions to the conformational energy and holding E_g fixed at the free chain value and $E_{g\mp g\pm} = 0$.

N	5	6	7	8
$\bar{u}_2/\mathrm{kJ\,mol^{-1}}$	5·9 (±0·6)	5·7 (±0·4)	5·1 (±0·4)	5·0 (±0·4)
$(\bar{u}_2)_{\mathrm{NI}}/\mathrm{kJ\,mol^{-1}}$	6·1	5·7	5·2	4·7
$\langle Y_{\mathrm{core}}\rangle_{\mathrm{NI}}$	0·45	0·39	0·43	0·37
$\langle S^*\rangle_{\mathrm{NI}}$	0·38	0·32	0·34	0·29
$Ds_{\mathrm{NI}}/\mathrm{J\,mol^{-1}\,K^{-1}}$	3·2	2·5	2·4	1·8
$E_g = 2\,\mathrm{kJ\,mol^{-1}}$		$E_0^{(1)} = 0{\cdot}32\ (\pm 0{\cdot}07)\,\mathrm{kJ\,mol^{-1}}$		$h = 0{\cdot}26\ (\pm 0{\cdot}05)$

the core by its centre of mass (determined from the core geometry implied by X-ray measurements [22]). The resulting N.M.R. fits are slightly improved even though the procedure is now more restrictive since the orientational order in the nematic phase of the homologous series is reproduced in terms of just the three constants $\bar{u}_2$, h and $E_0^{(1)}$. The overall variation found for these quantities is again below 30 per cent. Whilst the details of the order parameter profiles resulting from the two calculations are different, the tendency of the average accuracy to improve with increasing T and N persists. We consider this to be an indication that the spherical approximation to g_0 grows worse for shorter and/or better aligned chains.

The phase transition values of the order parameters and the entropy exhibit the even–odd effect but other than that there are noticeable qualitative differences between the results of the two calculations reflecting the sensitivity of the nematic–isotropic predictions to the choice of the conformational energy.

5. Concluding remarks

The primary conclusion drawn from these calculations is that the intermolecular interactions do modify appreciably the free chain conformational energy, and that the effects of such modifications can be reasonably accounted for by means of a single interaction strength parameter. In addition, it is worth noting the following.

(i) As a result of the low values of $E_{g^{\mp}g^{\pm}}$, the $g^{\mp}g^{\pm}$ sequences appear to be more abundant in the interacting chain in spite of the fact that they produce quite the opposite of the elongated molecular shape that favours nematic order. This can be understood qualitatively as reflecting the conflict between the forces preventing intermolecular overlap and those preventing internal overlap (i.e. between segments of the same molecule), in the sense that internal overlap reduces in general the effective size of the molecule and thus makes intermolecular overlap less probable.

(ii) A comparison between the results of tables 1 and 2 indicates that the values of the constant h and also the calculated values of entropy changes and order parameters at the nematic–isotropic transition are sensitive to the choice of the form of $E(n)$. The N.M.R. measurements, however, were reproduced to essentially the same accuracy (10 per cent) in both cases. Accordingly, a higher level of accuracy is required in order to reach definite conclusions on the details of the interaction mechanism and to make firm qualitative predictions concerning the phase transition.

(iii) Refinements such as the inclusion of biaxial interactions, the use of more than three rotational states, corrections to the tetrahedral geometry and taking into account the intramolecular core–chain interactions can improve the accuracy of the fits. Major improvements, particularly in the transferability of the basic parameters between members of the homologous series, should be expected, however, if a more realistic (i.e. orientation and conformation dependent) form of $g_0(x, x')$ is used to perform the averaging in equation (13). Clearly the assumption of a spherically symmetric g_0 gives a rather distorted representation of the repulsive intermolecular forces and furthermore introduces an implicit dependence of the interaction parameters on the effective molecular radius R_0, whose variation with chain length and temperature can only be treated as empirical input to the theory. The need for a more realistic consideration of the effects of short range repulsions is also suggested by the results of fits to N.M.R. data on n-alkanes in nematic solvents [9].

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