

The conformations of alkyl chains in fluids. A maximum entropy approach

R. Berardi, F. Spinuzzi, C. Zannoni

Dipartimento di Chimica Fisica ed Inorganica, Università, Viale Risorgimento, 4, 40136 Bologna, Italy

Received 5 June 1996; in final form 1 August 1996

Abstract

We present a maximum entropy internal order method for analyzing chain conformations in liquid crystalline solutions. We show how *prior* knowledge of the conformational distribution can be taken into account and apply the method to the determination of the conformation of *n*-alkanes in liquid crystals without invoking molecular field or other approximate theoretical models.

Alkyl chains are an essential component of membranes and of many polymers and liquid crystals where they typically confer fluidity. The determination of the conformational distribution of alkyl chains is an important but still largely unsolved problem attacked with a number of experimental techniques [1]. NMR is a particularly important structural tool and both deuterium (^2H NMR) and proton (^1H NMR) NMR are often employed for flexible molecules [2]. The proton NMR technique in liquid crystal solvents (LX NMR) is potentially more informative. In fact, the nuclear dipolar coupling D_{ij} between a pair of nuclei i, j with gyromagnetic ratios γ_i, γ_j depends on the interatomic distance r_{ij} and the molecular geometry [2]

$$D_{ij} = -\left(h\gamma_i\gamma_j/4\pi^2\right)\langle P_2(\cos \theta_{ij})/r_{ij}^3 \rangle, \quad (1)$$

where θ_{ij} is the angle between the internuclear vector r_{ij} and the magnetic field direction and $\langle \dots \rangle$ indicates an orientational–conformational ensemble

average. For a flexible molecule, r_{ij} and θ_{ij} will depend, in general, on the structure of the molecule and at least certain dipolar couplings will be modulated by configurational changes. The number of D_{ij} rapidly increases with the complexity of the molecule, making their determination difficult. However, recent elegant random deuteration NMR experiments [3] have provided proton dipolar couplings for *n*-alkanes in a liquid crystal solvent and new experimental developments offer heteronuclear [4] or ^{13}C – ^{13}C dipole couplings also for complex liquid crystals and lipids [5].

On the other hand, the increasing availability of these experimental data does not directly translate to conformational information. The structural information is normally extracted fitting conformational parameters to the observables, with the help of approximate theoretical treatments [6–10]. These are typically mean field (MF) approaches that consider a single molecule in an effective molecular field, while each conformer is treated as a biaxial molecule

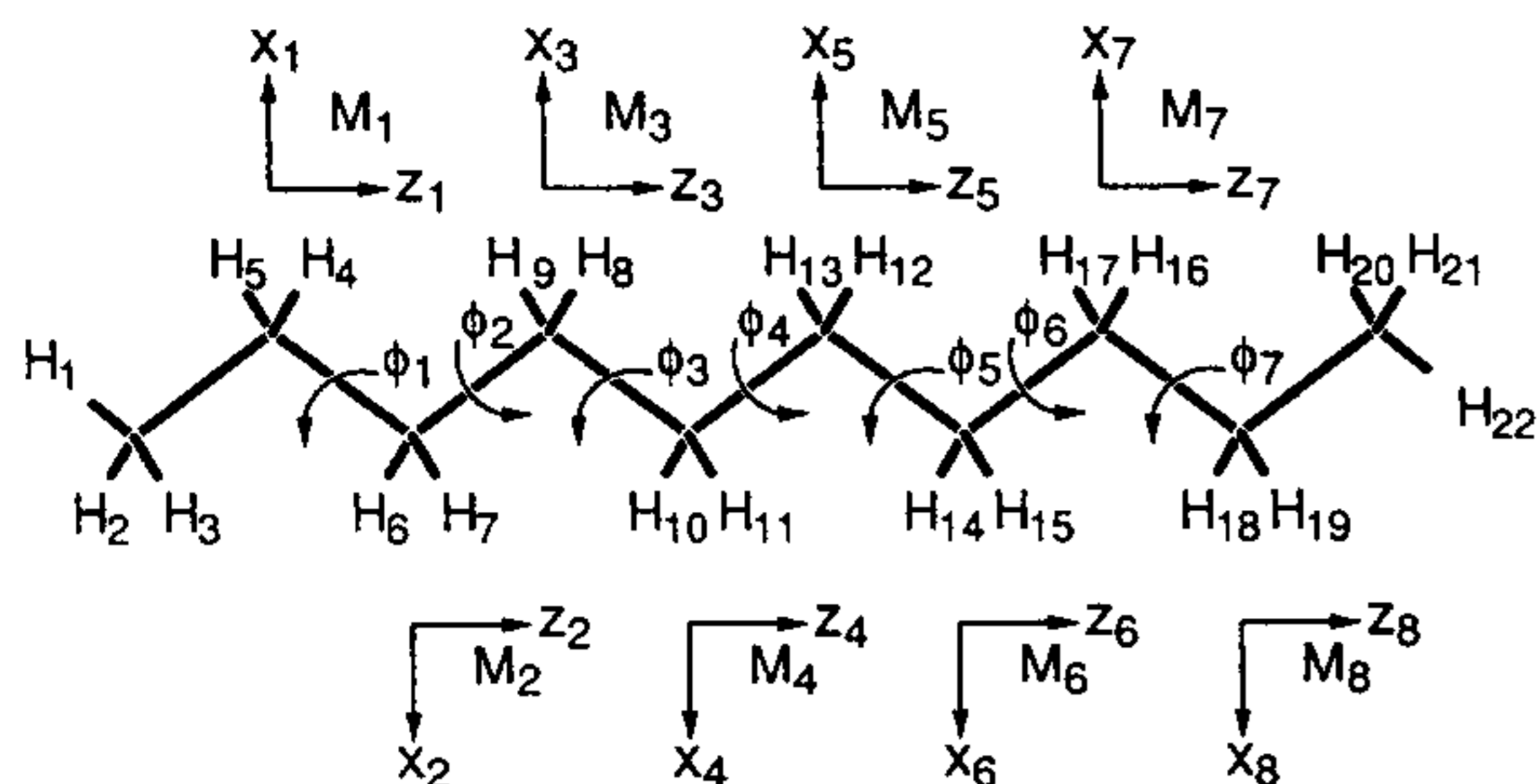


Fig. 1. The location and orientation of the local rigid fragment coordinate frames M_k , the internal angles ϕ_k and the proton numbering scheme adopted for n -alkanes (n -decane shown). Each conformer is identified by the set of internal angles $(\phi_1, \phi_2, \dots, \phi_{N-1}) \equiv \{\phi\}$ using the conformation $(0, 0, \dots, 0) \equiv \{0\}$ as the reference one.

[7,9,10]. However, MF models are known to have limitations even for rigid molecules. For instance, the order parameters of a molecule like pyrene are found to vary with solvent [11] rather than being a property of the molecule itself as expected from MF theory [12] and there is no reason to believe that the agreement should be better if we have a rigid conformer rather than a true rigid molecule.

We have presented elsewhere [13–15] a framework for describing the ordering of molecules with internal degrees of freedom which considers a non-rigid molecule as a collection of rigid fragments with a distribution of interfragment angles (see Fig. 1). The “best” (in the sense of least biased) distribution compatible with the set of data is then obtained [14,15] using the maximum entropy principle [16]. We have used this approach to obtain the inter-ring dihedral angle distributions for various two ring molecules in nematic solvents [13,15].

Here we generalize the method to handle chain molecules. We treat a methylene chain as a set of N rigid fragments linked by $N - 1$ bonds [3] (see Fig. 1). The conformation of each bond is defined by a dihedral angle ϕ_i . The overall conformational state is defined as $(\phi_1, \phi_2, \dots, \phi_{N-1}) \equiv \{\phi\}$. The Euler angles $(\alpha, \beta, \gamma) \equiv \omega$ [18] describe the rotation from the laboratory system DIR with the Z axis along the director to frame M_1 and define accordingly the orientation of the molecule. For this $N - 1$ rotor system the average in Eq. (1) is determined by the

true singlet orientational–conformational distribution $P(\omega, \{\phi\})$

$$D_{ij} = -\frac{h\gamma_i\gamma_j}{4\pi^2} \int d\{\phi\} \int d\omega \frac{P_2(\cos \theta_{ij})}{r_{ij}^3} \times P(\omega, \{\phi\}). \quad (2)$$

In turn we try to approximate the true $P(\omega, \{\phi\})$ from the observable data. Since any one set of data is necessarily limited, this nearly impossible task is somewhat facilitated by any *prior* [19] (intrinsic) information $P_i(\{\phi\})$ we may have on the chain, based on previous independent investigations. In this case, following a Bayesian approach [19]

$$P(\omega, \{\phi\}) = (1/Z) P_i(\{\phi\}) P_e(\omega, \{\phi\} | P_i). \quad (3)$$

The second term P_e is the *external* (posterior) distribution that we estimate applying the maximum entropy principle to the analysis of experimental data. The constant Z allows for the distributions to be separately normalized. P_i could be determined at the minimum by the basic connectivity and skeleton geometry, resulting in certain conformations being forbidden. In this case $P_i(\{\phi\}) = f_i(\{\phi\})$ where the filter function f is zero or one if a conformation is sterically hindered or not. Forbidden conformations could be calculated once and for all and discarded checking, for example, whether the distance r_{kl} between a pair of atoms $\{k, l\}$ belonging to fragments M_i, M_j and separated by at least four atoms ($|i - j| \geq 4$) is lower than the sum of their van der Waals radii $r_{kl} \leq r_k^{(v)} + r_l^{(v)}$ (we assume $r_C^{(v)} = 1.7 \text{ \AA}$ and $r_H^{(v)} = 1.2 \text{ \AA}$ and bond distances and angles as in Ref. [3]).

It is important to notice that Eq. (3) is an ansatz for the full singlet distribution and not a mean field expression. Only when no input data is available and the information reduces to the prior one the full n -particle distribution becomes a product of single particle terms as in mean field theory. When data are available the P_e extracted will describe how the liquid crystal solvent or other solute molecules affect the actual configurations $(\omega, \{\phi\})$, given the underlying constraint P_i for the isolated molecule. That this is so is guaranteed by the fact that the actual determination of the distribution depends on an inversion of experimental data that are affected by all

the various types of correlations present in the fluid. Eq. (3) only restricts the functional form of the singlet distribution to be compliant also with what is known beforehand, in particular, the fact that a certain conformation is physically admissible in terms of steric repulsion. Looking for additional information prior to a new experiment, we recall that an important established knowledge on alkyl chains is summarized in the rotameric isomeric state (RIS) model of Flory [20]. For alkyl chains the angles ϕ_k take in the RIS approximation only three discrete values $\phi_k^{(j)}$ or, more simply j_k . These angles correspond to the trans, gauche⁺ and gauche⁻ local conformations of the alkyl chain. The three states can be assumed to have the same a priori probability or, more generally the energy E_{g_k} of a gauche with respect to trans for one or more conformational bonds k can be known from separate previous studies. Using the RIS approximation the orientational-conformational distribution (3) becomes

$$P(\omega, \{j\}) = (1/Z) P_i(\{j\}) P_e(\omega, \{\psi\} | P_i). \quad (4)$$

The *intrinsic* distribution is non-negative and normalized to one and can be written in this case as

$$P_i(\{j\}) \propto f(\{j\}) \exp\left(\sum_{k=1}^{N-1} E_{g_k}^* \delta_{j_k,t}\right), \quad (5)$$

where $E_{g_k}^* = E_{g_k}/k_B T$ at temperature T (k_B is the Boltzmann constant) and $\delta_{j_k,t} = 1$ if the state is t (trans) and zero otherwise. We do not make further assumptions such as the often used united atoms approximation which collapses a methylene in a single group.

The orientational-conformational distribution for a conformer in a uniaxial phase, $P(\omega, \{j\})$, can be expanded in an orthogonal basis of Wigner functions $D_{0,n}^L(\omega)$ [14,18]. Averages over this distribution imply integration over orientations and a sum of the allowed conformational states $\{j\}$. The expansion coefficients $p_{0,n;\{j\}}^L$ are the order parameters of the molecule in the conformation $\{j\}$. In particular, for each fragment M_k , we recover the purely orientational order parameters $S_{ZZ} = \langle P_2 \rangle$, $S_{XX} - S_{YY} = \sqrt{6} \text{Re} \langle D_{0,2}^2 \rangle$ and $S_{XZ} = \sqrt{3/2} \text{Re} \langle D_{0,1}^2 \rangle$, where S_{ij} are the components of the Saupe ordering matrix [14]. The order parameters $\langle D_{0,n}^2 \rangle_{M_k}$ of the fragment M_k are related to the $p_{0,n;\{j\}}^2$ by straightforward

geometrical transformations and represent all that is needed to calculate single particle and bond observables.

The N_C measured dipolar couplings D_{ij} can be written in term of irreducible tensors [14,18] as $\langle [T_{ij}]_{\text{MAG}}^{2,0} \rangle = \sqrt{3/2} D_{ij}$. The rotation from magnetic (MAG) field to director frame (DIR) just gives a scaling factor [13], while the dependence on molecular orientations and conformations emerges transforming to the M_1 frame placed on the first fragment. Introducing couplings $[T_I^S]_{\text{DIR}}^{2,0}$ symmetrized over all the equivalent nuclear pairs $I \equiv \{i, j\}$ [13] we find

$$\begin{aligned} \langle [T_I^S]_{\text{DIR}}^{2,0} \rangle &= \sum_{n=-2}^2 \langle D_{0,n}^{2,*}(\omega) [T_I^S]_{M_1}^{2,n}(\{j\}) \rangle \quad (6) \\ &= \sum_{n=-2}^2 \sum_{\{j\}} P_i(\{j\}) \\ &\quad \times \int d\omega D_{0,n}^{2,*}(\omega) [T_I^S]_{M_1}^{2,n}(\{j\}) \\ &\quad \times P_e(\omega, \{j\} | P_i). \quad (7) \end{aligned}$$

As long as $[T_I^S]_{M_1}^{2,n}$ is significantly modulated by the chain internal rotations we can try to recover some details of the unknown distribution $P(\omega, \{j\})$. The available information depends on the number of experimental nuclear couplings, N_C , but not all of these will necessarily add new structural information. Thus we first determine n_C (with $n_C \leq N_C$) linearly independent combinations $[t_I]_{\text{DIR}}^{2,0}$ of couplings by an orthogonalization procedure described in Ref. [13] (with a straightforward generalization to include a sum over discrete conformations weighted by P_i , cf. Eq. (7)) that discards combinations that have scalar products below a certain threshold. Thus, according to maximum entropy [16] the least biased approximation to the true distribution, obtained maximizing the entropy associated to P_e will be of the form [13,19]

$$\begin{aligned} P(\omega, \{j\}) &= (1/Z_0) f(\{j\}) \exp\left(\sum_{k=1}^{N-1} E_{g_k}^* \delta_{j_k,t}\right) \\ &\quad \times \exp\left(\sum_{I=1}^{n_C} \lambda_I [t_I]_{\text{DIR}}^{2,0}(\omega, \{j\})\right), \quad (8) \end{aligned}$$

where Z_0 is defined by the normalization condition. In practice we determine the best distribution, i.e. the

best set of Lagrange multipliers λ_i , minimizing a suitable “free energy” convex functional [13,17]. The effect of experimental errors is accounted for using a sampling method [13] to obtain a compatible

set of distributions and their average $\bar{P}(\omega, \{j\})$. The conformational distribution $\bar{P}(\{j\})$ is obtained integrating the full $P(\omega, \{j\})$ over orientations.

Pines and co-workers [3,21] have measured the

Table 1

MEIO analyses of experimental data by Rosen et al. [3] for *n*-alkanes from hexane to decane. For every molecule we report the 7 most frequent conformer types and their multiplicity m , the total (percentage) probability \bar{P} and the ratio $w_e \equiv P/P_i$. We use a prior $E_g = 2.1$ kJ/mol. A null m indicates a duplicate or non-existent conformation

		Hexane	Heptane	Octane	Nonane	Decane
t...t all-trans	m	1	1	1	1	1
	$\bar{P}(\%)$	19.8	12.6	8.0	5.2	3.7
	w_e	1.08	1.16	1.25	1.37	1.61
$g^\pm t...t$ end-gauche	m	4	4	4	4	4
	$\bar{P}(\%)$	32.2	19.7	12.0	7.6	5.0
	w_e	0.99	1.02	1.05	1.13	1.25
$tg^\pm t...t$	m	2	4	4	4	4
	$\bar{P}(\%)$	16.7	19.5	12.2	7.4	4.8
	w_e	1.02	1.01	1.07	1.10	1.20
$ttg^\pm t...t$	m	–	–	2	4	4
	$\bar{P}(\%)$	–	–	5.8	7.1	4.3
	w_e	–	–	1.02	1.06	1.08
$tttg^\pm t...t$	m	–	–	–	–	2
	$\bar{P}(\%)$	–	–	–	–	2.2
	w_e	–	–	–	–	1.10
$g^\pm g^\pm t...t$	m	4	4	4	4	4
	$\bar{P}(\%)$	14.1	8.2	4.9	3.0	–
	w_e	0.96	0.97	0.98	1.03	–
$tg^\pm g^\pm t...t$	m	–	2	4	4	4
	$\bar{P}(\%)$	–	4.0	–	–	–
	w_e	–	0.93	–	–	–
$g^\pm tg^\pm t...t$	m	2	4	4	4	4
	$\bar{P}(\%)$	6.9	8.2	4.8	–	–
	w_e	0.95	0.97	0.96	–	–
$g^\mp tg^\pm t...t$ end-kink	m	2	4	4	4	4
	$P(\%)$	7.0	8.4	5.2	3.2	2.0
	w_e	0.96	0.99	1.04	1.10	1.18
$tg^\mp tg^\pm t...t$	m	–	–	2	4	4
	$\bar{P}(\%)$	–	–	–	3.2	2.0
	w_e	–	–	–	1.10	1.18
$g^\pm g^\pm g^\pm t...t$	m	2	4	4	4	4
	$\bar{P}(\%)$	3.3	–	–	–	–
	w_e	1.00	–	–	–	–

proton dipolar couplings in a series of n -alkanes (hexane through decane) dissolved in the nematic p -pentylphenyl-2-chloro(4-benzylbenzoyloxy)-benzoate at a temperature scaled by that of the transition $T^* = 0.875 (T^* = T/T_{NI})$. They have found respectively $N_C = 10, 14, 15, 19, 20$ couplings going from hexane to decane. We have determined at first linearly independent combinations of these couplings, setting the threshold for discarding eigenvalues to 100 Hz for all the alkanes and $T = 314.1, 309.7, 308.2, 306.9, 304.8$ K [3] and finding $n_C = 8, 10, 11, 13, 14$ combinations respectively. We have then performed a MEIO analysis assuming a fairly generally accepted [20,9] value of E_g , i.e. $E_g = 2.1$ kJ/mol as prior information (Table 1). We have found excellent agreement between the experimental couplings and those recalculated from the distribution obtained. The overall rms error is 1.76, 8.33, 1.60, 3.25, 2.26 Hz going from hexane to decane. Reducing the threshold to 20 Hz substantially increases the number of parameters but does not change the results. The errors in Table 1, determined with 300 samplings [13], affect the last digit shown. We have obtained a complete set of purely orientational second rank order parameters averaging over the conformations. In Fig. 2 we show as an example the “chord” order parameter [9] S_{ZZ} for the various fragments and notice the characteristic higher order in the middle of the chain.

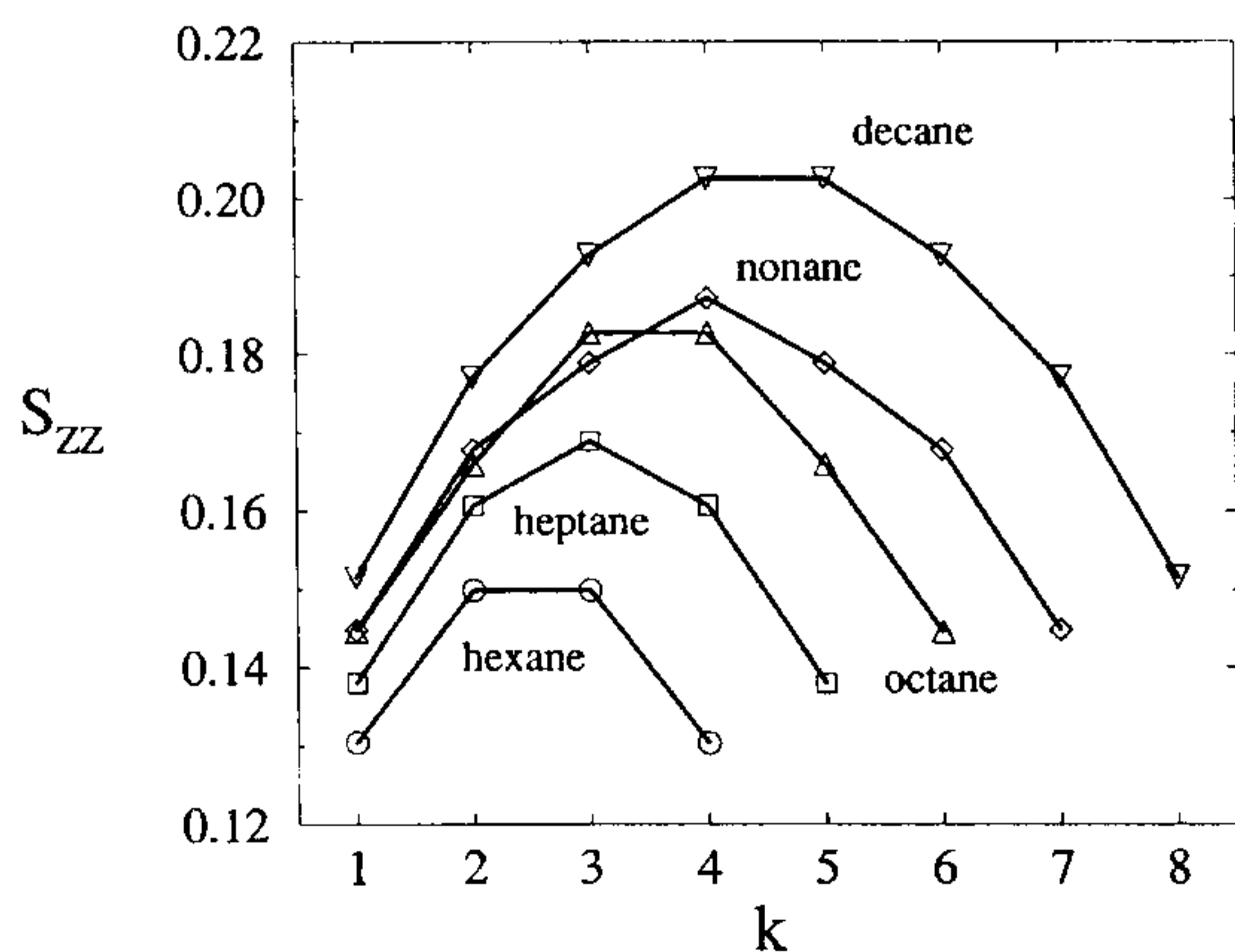


Fig. 2. The “chord” order parameters S_{ZZ} for fragment k of the chain obtained for the various n -alkanes analyzing Rosen et al. [3] NMR data with the MEIO procedure and a prior $E_g = 2.1$ kJ/mol.

We now turn to the conformational information. The number of non-sterically forbidden conformers is $n_T = 7, 13, 31, 65, 146$ for the various alkanes. We report in Table 1 the 7 most populated conformer types found for each alkane and we notice that they typically correspond to rather elongated conformers. Conformers with an end gauche defect are to within experimental error the most frequently occurring. P_i determines to a large extent what is obtained, as we see comparing the total \bar{P} and w_e , the ratio of \bar{P} to P_i . A value greater (lower) than 1 indicates that a conformer is favoured with respect to the prior and vice versa. We find (see Table 1) that the largest values of w_e are those for the all-trans conformers that increase with the length of the molecule.

To check the reliability of the MEIO method we have tested its ability to recover a conformer that is known to exist. Thus for every n -alkane we have performed an analysis starting from average dipolar couplings computed using a predetermined orientational-conformational distribution for all-trans (t...t) and terminal *kink* ($g^\mp tg^\pm t\dots t$) conformations corresponding to an orientational order similar to that of Rosen et al. [3]. The magnitude of the orientational order is of key importance since the effectiveness of the MEIO method decreases when the order is small [15]. The order parameters obtained using the MEIO analysis are essentially constant as expected for the all-trans and characteristically varying for the kink showing that even at the low order parameters of the experiment [3] these elongated conformations would be recognized. In the presence of a prior knowledge, as in the present case, the extra information carried by the data is manifested in w_e . The analysis of simulated data shows that w_e is in all cases dominant for the trans or respectively the kink conformer. Thus conformational information can be quite reliably obtained by MEIO even at these low order parameters.

Rosen et al. [3] have analyzed their data in terms of three MF models: an elastic continuum [8], a biaxial conformer [7,22] and the chord [9] model. In this last approach the orientation of neighboring pairs of C–C bonds induced by the nematic is considered and is shown to be accounted for by the alignment of the chord connecting these bonds [9]. Comparing the results in Ref. [3] for the probability

of one, two, etc., gauche defects with ours, we find that our results are in better agreement and tend to support the chord model. We only quote two instances. For hexane the total (percentage) \bar{P} of 0, 1, 2 gauche defects is, in our case, (19.8, 48.9, 28.0) and for the two parameter chord model [3] (20.0, 50.0, 27.0). Similarly, for decane we find (3.7, 16.3, 31.7), while Ref. [3] gives (4.0, 21.0, 35.0).

In summary, our results show that the MEIO method is able to analyze experimental data for molecules with many conformational degrees of freedom providing relevant structural information without recourse to approximate theories. The method does not assume the infinite dilution which is implicit in the MF analysis and can effectively provide conformational information even at the high solute concentrations (30 mol%) of Ref. [3]. This should open the possibility of studying, for instance, conformational changes as concentration changes. The probabilities for the different conformers shown in Table 1 can be refined as even more detailed data become available. We believe the method will be particularly useful for establishing chain conformations in smectic liquid crystals, in polymers and in biological membranes where higher orientational order can be achieved and that it will be a useful complement of the new experimental methods determining dipolar couplings.

We are grateful to CNR, MURST and CEC HCM programme for support. RB and FS thank the University of Bologna and INFN for postdoctoral fellowships.

References

- [1] Faraday Symposium 27 on The Conformation of Flexible molecules in Fluid Phases, *J. Chem. Soc. Faraday Trans. 88* (1992).
- [2] J.W. Emsley, ed., *Nuclear magnetic resonance of liquid crystals* (Reidel, Dordrecht, 1985).
- [3] M.E. Rosen, S.P. Rucker, C. Schmidt and A. Pines, *J. Phys. Chem.* 97 (1993) 3858; M.E. Rosen, Ph.D. Thesis, U.C. Berkeley (1992).
- [4] K. Schmidt-Rohr, D. Nanz, L. Emsley and A. Pines, *J. Phys. Chem.* 98 (1994) 6668.
- [5] D. Sanström, K.T. Summanenand and M.H. Levitt, *J. Am. Chem. Soc.* 116 (1994) 9357.
- [6] S. Marčelja, *J. Chem. Phys.* 60 (1974) 3599.
- [7] J.W. Emsley and G.R. Luckhurst, *Mol. Phys.* 41 (1980) 19; J.W. Emsley, G.R. Luckhurst and C.P. Stockley, *Proc. Roy. Soc. A* 381 (1982) 117.
- [8] A.J. Van der Est, M.Y. Kok and E.E. Burnell, *Mol. Phys.* 60 (1987) 397.
- [9] D.J. Photinos, E.T. Samulski and H. Toriumi, *J. Phys. Chem.* 94 (1990) 4688, 4694.
- [10] A. Ferrarini, G.J. Moro, P.L. Nordio and G.R. Luckhurst, *Mol. Phys.* 77 (1992) 1.
- [11] G.N. Shilstone, C. Zannoni and C.A. Veracini, *Liq. Cryst.* 6 (1989) 303.
- [12] G.R. Luckhurst, C. Zannoni, P.L. Nordio and U. Segre, *Mol. Phys.* 30 (1975) 1345.
- [13] R. Berardi, F. Spinozzi and C. Zannoni, *J. Chem. Soc. Faraday Trans. 88* (1992) 1863; *Liq. Cryst.* 16 (1994) 381.
- [14] C. Zannoni, in: *Nuclear magnetic resonance of liquid crystals*, ed. J.W. Emsley (Reidel, Dordrecht, 1985).
- [15] L. DiBari, C. Forte, C.A. Veracini and C. Zannoni, *Chem. Phys. Lett.* 143 (1987) 263; D. Catalano, L. DiBari, C.A. Veracini, G.N. Shilstone and C. Zannoni, *J. Chem. Phys.* 94 (1991) 3928.
- [16] R.D. Levine and M. Tribus, eds., *The maximum entropy formalism* (MIT Press, Cambridge, MA, 1979).
- [17] N. Agmon, Y. Alhassid and R.D. Levine, *J. Comp. Phys.* 30 (1979) 250; L.R. Mead and N. Papanicolau, *J. Math. Phys.* 25 (1984) 2404.
- [18] M.E. Rose, *Elementary theory of angular momentum* (Wiley, New York, 1957).
- [19] B.R. Frieden, in: *Maximum-entropy and Bayesian methods in inverse problems*, eds. C.R. Smiths and W.T. Grandy Jr. (Reidel, Dordrecht, 1985).
- [20] P. Flory, *Statistical mechanics of chain molecules* (Wiley Interscience, New York, 1969).
- [21] M. Gochin, A. Pines, M.E. Rosen, S.P. Rucker and C.S. Schmidt, *Mol. Phys.* 69 (1990) 671.
- [22] B. Janik, E.T. Samulski, D.J. Photinos and H. Toriumi, *J. Phys. Chem.* 91 (1987) 1842.