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Reply to "Comment on the NMR determination of molecular order in the smectic-*C* phase"

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A rigorous description of the NMR data in the smectic-*C* phase in terms of eight order parameters that are given in the preceding Comment by A. Wulf is not possible and does not include all of the information the experiment provides. Furthermore, the failure of two order parameters to satisfy a functional inequality is not due to excessive or redundant order parameters as implied in the Comment, but to a lack of precise values for conformational coefficients. The segmental order parameters directly measured in the NMR experiment and their relationship to global molecular order is discussed here more completely.

We believe that the reasoning presented by Wulf does not fully take into account the complications that arise from the fact that in the smectic-*C* (S_C) phase of heptyloxyazoxybenzene (HOAB-d_{30}) one has to deal with anisotropic fluctuations of flexible noncylindrically symmetric molecules. As a result, his reasoning is directly applicable only in the case where all the deuterated sites in the molecule share a common principal axis relevant to the time-averaged NMR spectra. This condition is obtained in the nematic phase of the compound, and there the nonvanishing order parameters are just two, namely, S_{00} and S_{02}. In the S_C phase, where there is not a common NMR principal axis,[1,2] a rigorous description of the molecular order in terms of eight (or nine or any other number) global molecular order parameters is not possible for practical reasons and, furthermore, does not include all the physical information that the experiment provides.

We think, instead, that a natural description of the molecular order in the S_C phase is in terms of segmental order parameters and local principal-axis frames whose relative orientations are directly measurable. The global order parameters are thereby obtained indirectly, by making some further statistical assumptions for the purpose of establishing a simple connection between segmental and global order parameters, and by specifying through such assumptions a molecular frame M fixed with the "rigid" part or most ordered segment of the molecule. In what follows we will give some clarifying details of this situation.

Consider a frame N, fixed with the liquid-crystal phase, defined by taking its x_N axis to be normal to the plane of symmetry of the (apolar) S_C phase and z_N to be the axis of alignment of the stationary sample in the magnetic field $\vec{H}$. In the spinning sample experiments, it turns out that the direction of $\vec{H}$ remains in the plane $z_N y_N$. In that case the NMR splitting of the ith molecular site is given by

$$\delta\nu_i = 2\nu_Q[e_i + f_i \cos 2(\theta_0 + g_i)] , \qquad (1)$$

where $e_i = \frac{1}{8}(A_i - 2B_i)$, $f_i = [C_i^2 + (\frac{3}{4}A_i + \frac{1}{2}B_i)]^{1/2}$, $g_i = \frac{1}{2}\sin^{-1}(C_i/2f_i)$, and $A_i = \frac{3}{2}\langle\frac{3}{2}\cos^2\sigma_i - \frac{1}{2}\rangle$, $B_i = \frac{9}{8}\langle\sin^2\sigma_i \cos 2\xi_i\rangle$, $C_i = \frac{9}{8}\langle\sin 2\sigma_i \sin\xi_i\rangle$. The angle θ_0 is the polar angle of $\vec{H}$ and σ_i, ξ_i are the polar and azimuthal angles of the direction z_i of the C-D (or C–CD$_3$) bond in the frame N. In Eq. (1) we have assumed that the local asymmetry of η_i^s of the electric field gradient as measured in the solid phase vanishes.

The spectral patterns of the spinning sample give directly the quantities e_i and f_i is obtained from the splitting of the aligned sample.[2] Physically g_i is the angle between z_N and the axis $z_{\tilde{N}_i}$ of the local principal-axis frame $x_{\tilde{N}_i} \parallel x_N, y_{\tilde{N}_i}, z_{\tilde{N}_i}$ of the ith site. The defining condition for this frame is $\tilde{C}_i = \frac{9}{8}\langle\sin 2\tilde{\sigma}_i \sin\tilde{\xi}_i\rangle = 0$. It turns out that different molecular sites exhibit, in general, different values of g_i which are also *temperature dependent*. Thus, a complete description of the molecular order in terms of spinning sample NMR measurements consists of obtaining at each temperature point a set of three quantities for each molecular site. There are two equivalent choices for this set:

(a) A_i, B_i, C_i, if one measures the fluctuations of z_i for all sites in a common frame which, for convenience, we take to be the frame N.[1]

(b) $\tilde{A}_i$, $\tilde{B}_i$, g_i, if one measures the fluctuations of z_i in the respective principal-axis frame $\tilde{N}_i$. In this case g_i gives the orientation of each principal $z_{\tilde{N}_i}$ axis relative to z_N.[2]

In either case, all frames are well defined and the quantities are directly measurable and have a clear physical significance. There are no redundant quantities and no ambiguities (except probability in the relative signs of e_i, f_i which can usually be resolved in an obvious way). There is a freedom in choosing the z_N axis, which in principle could be chosen at will since what matters are the relative orientations of the local $z_{\tilde{N}_i}$ axis. The most convenient choice is, however, the one we made since, as it turns out, all the $z_{\tilde{N}_i}$ axes, except those of the terminal methyl group, are along the direction of alignment of the stationary sample.[2]

To deduce from the segmental order parameters A_i, B_i, C_i the values of the global order parameters S_{ab}, one usually assumes that the conformational fluctuations are statistically independent of the global molecular fluctuations. This assumption allows us to express in a simple way S_{ab} in terms of A_i, B_i, C_i and the conformational averages r_i, s_i, t_i as in Eq. (20b) of Ref. 1. The order parameters S_{ab} describe the fluctuations of the molecular frame M as measured in the frame N.

To apolar phases the axis x_M is defined as the axis of polar (statistical) inversion. The axis z_M, however, does not have an obvious definition unless the molecular motion has a twofold or higher symmetry of rotation about an axis perpendicular to x_M. It turns out that in the S_C phase such an axis of rotation does not exist.[1,2]

To each choice of z_M corresponds a different set of S_{ab} and r_i, s_i, t_i, but the order parameters A_i, B_i, C_i remain invariant. In Ref. 1, a direction for z_M was singled out by taking $s_1=s_2$, $t_1=t_2$, and by assigning particular values to r_1 and r_2. These assignments could or could not result in $S_{10}=0$ but in any case they constitute a specification of the frame M. In fact, they might constitute an overspecification of M since the assignments of particular values to r_1 and r_2 were not made on the basis of a detailed calculation that would take into account the conformational averages of all the deuterated molecular sites, but rather on the rough basis of requiring that S_{00} and z_0 assume certain values at certain temperatures as described in Ref. 1.

An alternative but equivalent way to single out a direction for z_M would be to define it as the axis that gives the maximum value of S_{00}, or that gives $S_{10}=0$, etc. But in this case one would still have to find a way of determining the values of the conformational averages in the so defined M frame. Thus, in practice the specification of the frame M is inevitably influenced to some extent by the assumption of statistical independence of conformational and molecular fluctuations.

From the above it becomes apparent that the failure of the plots of S_{00} and S_{20} to satisfy the inequality $S_{20}\leq\frac{2}{3}(1-S_{00})$ is not related to excessive or redundant order parameters, or to incompletely defined frames. Rather, it is a result of the lack of precise and mutually consistent values of the conformational averages that forces one to resort to rough estimates.

Of course, the discrepancy between S_{00}, S_{20} can be trivially removed by choosing a slightly larger value for $|r_1-r_2|$, which would result in a simultaneous uniform rescaling of S_{00} and S_{20} (and S_{10}) to any desired value. In particular, if instead of the value of 0.04 of Ref. 1, one takes any value for $|r_1-r_2|\geq 0.055$ the discrepancy between S_{00}, S_{20} disappears with S_{10} still nonvanishing. What is more interesting is to determine the significance of incompatibility errors of the values of r_i, s_i, t_i in the determination of the order parameters S_{ab}.

An assignment of a particular value to r_1-r_2 determines the frame M. In this frame s_1, t_1 may or may not be equal to s_2, t_2. Consider now the equations

$$\frac{2}{3}(A_1-A_2)=(r_1-r_2)S_{00}+\frac{3}{4}(s_1-s_2)S_{0,2}+\frac{3}{4}(t_1-t_2)S_{01} \qquad (2)$$

and

$$\frac{8}{9}(B_1-B_2)=(r_1-r_2)S_{20}+2(s_1-s_2)S_{22}-\frac{3}{2}(t_1-t_2)S_{2,1}\,. \qquad (3)$$

If (s_1-s_2) and (t_1-t_2) are of the order of (r_1-r_2) we may still make the approximation $s_1\simeq s_2$, $t_1\approx t_2$ and determine S_{00} from Eq. (2) without significant error since S_{00} is large compared to S_{02}, S_{01}. The same approximation, however, would result in large errors where S_{20} is determined from Eq. (3). This is because in the absence of rotational symmetry in the molecular motion, the order parameters S_{20}, S_{22}, S_{21} are of the same order of magnitude.

These problems, of course, are not encountered in the nematic phase where only S_{00} and S_{02} are nonvanishing.

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[1] D. J. Photinos, P. J. Bos, M. E. Neubert, and J. W. Doane, Phys. Rev. A 20, 2203 (1979).

[2] D. J. Photinos, P. J. Bos, M. E. Neubert, and J. W. Doane Phys. Rev. A (in press).