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Neutron scattering study of the hydration hull of DNA by H_2O/D_2O -exchange

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Abstract

Films of highly oriented DNA (A-, B-, and C-conformation) were investigated by neutron scattering. Diffuse sheets corresponding to a one-dimensionally periodic "water-DNA" structure are identified close to the intersection of the helix direction with the structure factor maximum of bulk water. The correlation length in this structure is strongly influenced by its commensurability with the axial translation H per nucleotide. The fiber or lateral chain interaction is enhanced in the commensurate case.

The important role of water in stabilizing the structures of DNA has been recognized by the variation of x-ray patterns with the humidity of the fiber¹. Many details have been investigated for a better understanding of this subtle interaction², i.e. by studies on hydration sites and binding energies³, on spine formation⁴ and the influence of counterions⁵ as well as by elucidating computer simulations⁶. First results of inelastic neutron measurements have been reported previously⁷. In the following, elastic (i.e. three axis spectrometer with resolution of 0.23 THz set to zero energy transfer) data are presented which allow the direct identification of water correlations in DNA fibers by means of H_2O/D_2O -exchange¹⁰.

We have re-investigated the C-DNA sample used earlier⁸ (the C-conformation has 9.3 nucleotide pairs in a pitch of $C_C = 30.9\text{\AA}$) and in addition two new samples (A- and B-conformation, 11 and 10 nucleotide pairs in a pitch of $C_A = 28.1$ and $C_B = 33.8\text{\AA}$, respectively). The different conformations were stabilized by the excess salt content⁵. It was $0.06NaCl$, $0.35LiCl$, and $0.03LiCl$ per nucleotide for the samples A, B, and C, respectively (named according to the typical x-ray pattern

for 75% relative humidity (r.h.))

The most likely region of reciprocal space (Q) for the detection of correlations between water and DNA is the intersection of the helix axis with the sphere of the first maximum in the structure factor of D_2O . This peak was observed at $\langle Q \rangle \simeq 1.96 \text{ \AA}^{-1}$ having a full width at half maximum (FWHM) of $\delta Q \simeq 0.7 \text{ \AA}^{-1}$ by filling the DNA container ($40 \times 40 \times 1 \text{ mm}^3$) with D_2O .

Fig.1 shows the measured intensity for the A-sample obtained for a scan along the helix axis (Q_{\parallel}) passing through this region. The sample was humidified to 75% r.h. both with H_2O and D_2O . The comparison proves that the peak at $\langle Q_{\parallel} \rangle \simeq 1.92 \text{ \AA}^{-1}$ ($\delta Q_{\parallel} \simeq 0.25 \text{ \AA}^{-1}$) is mainly due to water. A similar observation had been made previously for the C-sample⁸ but the lack of long range order of the sample allowed no comparison with DNA reflections in this Q-range. This is different here. The narrow peak at $\langle Q_{\parallel} \rangle = 2.46 \text{ \AA}^{-1}$ corresponds to the reflection $(0, 0, 11)_A$ of the A-conformation. Note the difference in the correlation lengths ($l_{\parallel} = 2/\delta Q_{\parallel}$) for this and the "water peak" (WP). Compared to bulk D_2O , however, this DNA-water is about three times "better" correlated. Further observations are that the position of the WP is *incommensurate* with C_A and that a fraction of the sample has the periodicity of B-DNA as indicated by the small $(0, 0, 10)_B$ peak at $Q_{\parallel} = 1.86 \text{ \AA}^{-1}$ on the flank of the WP. We have verified the monotonous increase of the WP with the D_2O -content of the sample as shown in Fig.2. In addition, one recognizes that the small B-DNA admixture becomes more pronounced at lower humidity and that the WP shifts to smaller momentum transfer at higher humidity ($\simeq 1.90 \text{ \AA}^{-1}$ as for C-DNA).

Actually, the WP represents an intersection through a *disklike* intensity distribution as has been found by mapping the scattering intensity in the entire Q_{\parallel}, Q_{\perp} region of the WP, i.e. the lateral extension and the curvature of the WP-ridge cannot be explained by the FWHM ($\simeq 5^\circ$) of the helix direction distribution.

Fig.3(a) shows this disk for the C-sample. It has been verified that this feature is absent for H_2O -humidification⁸. Remnants of broad Debye-Scherrer rings with texture indicate less ordered water and/or DNA. The disk is centered at $\langle Q_{\parallel} \rangle = 1.905 \text{ \AA}^{-1}$ having a "thickness" of $\delta Q_{\parallel} \simeq 0.09 \text{ \AA}^{-1}$ and a "diameter" of $\delta Q_{\perp} \simeq 0.74 \text{ \AA}^{-1}$. In real space, this disk corresponds to a density-density correla-

tion function $\rho(\mathbf{r}) = \rho_{\perp}(\mathbf{r}_{\perp}) * \rho_{\parallel}(r_{\parallel})$ which has the shape of a corrugated cylinder or a pyramid cake. The main periodicity of $\rho_{\parallel}(r_{\parallel})$ is $d_{\parallel} = 3.30\text{\AA}$ which is *incommensurate* with $C_C = 30.9\text{\AA}$. However, d_{\parallel} is close to $H_C = 30.9\text{\AA}/9.3 = 3.32\text{\AA}$. The "thickness" of the disk implies a correlation length $l_{\parallel} \simeq 20\text{\AA}$. From the "diameter" of the disk one may derive a rough estimate of the average diameter d_{\perp} of $\rho_{\perp}(\mathbf{r}_{\perp})$. A value of $d_{\perp} \simeq 9$ to 10\AA would follow from a cylinder of constant scattering density if the effective mosaic of the helix axis is varied from 0 to 20° . Modifications by models with two concentric cylinders of variable scattering density result in even smaller values of d_{\perp} .

One is, therefore, led to the conclusion that the water giving rise to the disklike scattering is located near the bottom of the helical grooves⁴, regardless whether one places the corrugated cylinder $\rho(\mathbf{r})$ between or at the helix axes positions. Its corrugation is close to H but the correlation length is less than C_C . Phenomenologically, the disklike scattering can be understood as the first sheet of a free 1-d chain being modulated by the formfactor due to the lateral extension of the chain, i.e.

$$S_{\perp}(\mathbf{Q}) = \left| \int e^{i\mathbf{Q}_{\perp}\mathbf{r}_{\perp}} \rho_{\perp}(\mathbf{r}_{\perp}) d\mathbf{r}_{\perp} \right|^2 \frac{\sinh\left(\frac{Q_{\parallel}^2 u^2}{2}\right)}{\cosh\left(\frac{Q_{\parallel}^2 u^2}{2}\right) - \cos(Q_{\parallel} d_{\parallel})} \quad (1)$$

with $u^2 = d_{\parallel}^3 / (2\pi^2 l_{\parallel})$.

The absence of "Bragg-reflections" on top of the disk corresponds to a vanishing correlation of neighboring chains in the helix direction (no phase lock-in). This latter aspect is qualitatively different in the case of the B-sample as shown in Figs.3(b-d). The scattering pattern obtained for this sample at 84% r.h. (Fig.3(b)) is qualitatively similar to that of the C-DNA sample at 75% r.h. Note, however, the different slope of the disk along Q_{\perp} which indicates a different amplitude of corrugation. The disk is now centered at $\langle Q_{\parallel} \rangle = 1.87\text{\AA}^{-1}$, i.e. very close to the commensurate value of $Q_{\parallel} = 1.86\text{\AA}^{-1} (= (0, 0, 10)_B)$. Its "thickness" corresponds to an increased correlation length of $l_{\parallel} \simeq 28\text{\AA}$.

The corresponding intensity pattern at 75% r.h. (Fig.3(d)) shows the effect of the phase lock-in (3-d ordering) by means of the "Bragg reflections" on top of the disk. The correlation length of $l_{\parallel} \simeq 45\text{\AA}$ is now larger than C_B and the position is commensurate. The reduction of the "diameter" of the disk to $\delta Q_{\perp} \simeq 0.57\text{\AA}^{-1}$

is compatible with the $\simeq 20\%$ increase of the lateral distance of the helices as compared to the C-DNA at 75% r.h. A significant part of the disk intensity is due to the correlated water as demonstrated by Fig.3(c).

The simultaneous presence of 1-d (disk) and 3-d features ("Bragg reflections") in the scattering pattern can be understood in terms of small crystallites embedded into regions of phase disordered chains. An alternative, spatially homogenous picture is the so called *weakly coupled chain array*⁹ which incorporates the effective lateral interaction $J(\mathbf{Q}_\perp)$ in mean field approximation, i.e.

$$S_3(\mathbf{Q}) = \frac{S_1(\mathbf{Q})}{1 - J(\mathbf{Q}_\perp)S_1(\mathbf{Q})} \quad (2)$$

Measurements with a new B-DNA sample having free standing films - allowing for *in situ* humidification - might give further insight into the applicability range of these two pictures.

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Figure captions

- Fig.1** - Intensity variation with momentum transfer parallel to the helix axis for the B-sample humidified to 75 % r.h. with D_2O (\circ) and H_2O (\square). The scale refers to the actually collected counts and the peak/background ratios are comparable, only. The peak at $Q_{\parallel} = 2.69 \text{ \AA}^{-1}$ is the (1,1,1)-Debye-Scherrer ring due to the Al-container and shows the Q_{\parallel} resolution.
- Fig.2** - Uncalibrated humidity variation of the scan through the WP. The A-sample was vacuum dried for five hours and then exposed to D_2O -humidified air ($\approx 90\%$ r.h.) during the measurement. The time scale refers to elapsed time after the first scan. Optimum A-DNA reflections were obtained for $1 \leq \text{time/hour} \leq 5$.
- Fig.3** - Projections of elastic scattering intensity mapped in Q -space parallel and perpendicular to the helix axis. (a) corresponds to C-sample at 75% r.h. D_2O ; (d) is like (a) for B-sample; (b) is like (d) for 84% r.h.; (c) is like (d) for H_2O . The intensities are normalized. (a) and (b) are enhanced by a factor of two. The pattern (d) had to be rotated by 5° because of inaccurate alignment of the sample.





