Slow Relaxation Process in DNA

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Abstract. A dynamic transition at temperatures $\sim$200–230K is observed in many hydrated bio-polymers. It shows up as a sharp increase of the mean-squared atomic displacements above this temperature range. We present neutron scattering data of DNA at different levels of hydration. The analysis shows that the dynamic transition in DNA is related to a slow relaxation process in the MHz-GHz frequency range. This slow relaxation process is completely suppressed in the dry DNA sample where no dynamic transition was observed. The nature of the slow process is discussed. We ascribe it to a global relaxation of DNA molecule that involves cooperative motion of many base-pairs and backbone.

Key words: Bio-polymers, dynamic transition, dynamics, influence of hydration, relaxation in bio-polymers

1. Introduction

Question of relations between dynamics and functions of proteins remains a puzzle. It is known that functions of bio-polymers require that the molecule will go through a few conformational states [1]. These conformational transitions will be suppressed if intrinsic motions of the molecule are suppressed. This naïve consideration gives an obvious argument that molecular motion influences strongly functions of biomolecules.

It was found that hydrated bio-polymers demonstrate sharp slowing down of their functions (kinetics of bio-chemical reactions) at temperature range $T\sim$250–200K [2,3]. Analysis of mean-squared atomic displacement, $<x^2>$, demonstrates sharp rise around that temperature range [2–6]. The sharp increase in $<x^2>$ was found in all hydrated bio-polymers investigated so far and was attributed to some dynamic transition in bio-polymers at this temperature range. In most of the papers, the authors ascribe the transition to strong rise of anharmonicity of the molecular motion [2, 3]. Coincidence of characteristic temperatures for the slowing down of bio-chemical activities and for the dynamic transition suggests a direct relation between these two events. Later on, it was demonstrated that the dynamic transition can be suppressed in dry bio-polymers [4], or in bio-polymers dissolved in trehalose [7]. Moreover, it can be shifted to higher temperature for

proteins dissolved in glycerol [6]. Thus the dynamic transition can be controlled by changing the surrounding of the bio-polymer.

However, the dynamic transition in most cases was identified by an analysis of $<x^2>$ obtained from neutron or X-ray scattering, or from Mossbauer spectroscopy [2–7]. This integrated quantity does not allow detailed analysis what is really happening with bio-polymers around this temperature range, what kinds of motion or relaxation process is activated around the dynamic transition.

That is the main goal of the paper to present a detailed analysis of neutron scattering data measured with high energy resolution. The measurements have been done in a broad temperature range for three Li-DNA samples with different hydration levels. We were able to suppress the dynamic transition by changing humidity. The results of the data analysis show that the dynamic transition is related to suppression of a slow relaxation process and not to anharmonicity of the molecular motion in general. The nature of the slow process is discussed. We ascribe it to a global relaxation of the bio-molecule. A short account of this work has been published in [8].

2. Experimental

Li-DNA fibers hydrated with D_2O to three different levels of hydration were used for the measurements. The samples consist of zig-zag folded films of wet spun fibers [9] originating either from calf-thymus (Worthington Biochemical) or salmon testes (Fluka). The desired levels of hydration were achieved by storage of the samples over saturated D_2O-solutions of KBr (81% r.h., 'hum'-sample), $NaClO_3$ (75% r.h., 'opt'-sample) and LiCl (11% r.h., 'dry'-sample). All three samples have been characterized previously in neutron scattering studies of distinct correlations [10,11]. Due to their excess salt content of 0.7LiCl/bp they adopt the B-conformation at optimum humidity (66–75%). The weights on sealing the samples in flat Al containers were 1.6687 (hum-), 2.0327(opt-), and 1.3551g (dry-sample). The relative weight of water per dry DNA was estimated on the basis of weight control during changes of humidity, measured cross sections and comparison to the data of Lindsay et al.[12]. The resulting relative weights of water per dry DNA are: 0.655±0.004 for the 'hum', 0.455±0.004 for the 'opt', and 0.026±0.004 for the 'dry' samples. This entails 21.4 to 21.7 D_2O-molecules per basepair (bp) for the 'hum'-sample. The corresponding figures for the 'opt'-sample are 14.8 to 15.1/(bp) and 0.7 to 1.0/bp for the 'dry'-sample.

Neutron scattering spectra were measured on IN5 time-of-flight spectrometer at ILL, Grenoble, France. Two different wavelength, $\lambda = 5\text{Å}$ and $\lambda = 8\text{Å}$, were used in order to obtain good resolution at lower energy and reasonable statistics at higher energies. The measured spectra were corrected for the wavelength dependence of detectors, empty can, and corrected for self-absorption and multiple-scattering in the quasi isotropic approximation. After calibration by the Vanadium scan, the resulting spectra were summed up over the angular range $56° < \Theta < 126°$ and scaled by

the scattering cross section of the various samples. Due to the dominant incoherent scattering contributions of hydrogen, the spectra shown below thus represent the angular averaged scattering cross section per hydrogen. No essential information is lost by the angular averaging since the shape dependence on the momentum transfer Q is monotonous and weak. Considering the range of energy transfers from elastic scattering up to 2.2THz, the spectra correspond to momentum transfers Q of 1.2 to 3.3Å^{-1} in the case of $\lambda = 5$Å and 0.8 to 2.8 Å^{-1} for $\lambda = 8$Å.

In addition, high-resolution spectra were measured on the back-scattering spectrometer BSS-FZJ (Juelich, Germany) for the same samples. The spectral resolution is 2 μeV or 0.5GHz. The incident wavelength is 6.37Å. The spectra were summed over the angular range $68° < \Theta < 160°$ and correspond thus to momentum transfers Q between 1.1 and 2 Å^{-1}. The spectra were corrected for the instrumental background and sample container. The instrumental background is dominated by neutrons which have not passed the analyzer crystals. This contribution was determined separately by covering the analyzer with the strong absorber Cd and identical conditions otherwise. An additional 'opt'-sample was prepared having half the mass and thickness of the original sample in order to investigate the influence of multiple scattering experimentally. Comparison of those two sets of data exhibited no difference within statistics.

An advantage of neutron scattering spectroscopy is that it measures molecular motion directly. The motion of hydrogen atoms gives the main contribution to the neutron scattering spectra due to the extremely large incoherent scattering cross-section of H-atoms (at least 10 times large than any other atoms and ~40 times large than deuterium). It is believed, however, that in the frequency range of interest, $\nu < 3$THz (E<10meV, that is ~100 times slower than the vibration of single H-atom) the motion of hydrogen atoms reflects cooperative motion of large groups of atoms. In fact, the low energy response due to local vibrations, i.e. the librational spectra in the range 40meV<E<75meV provide a control for the humidification status of the samples. The strong difference in scattering cross-section between H and D atoms leads to negligible contribution of D_2O to our spectra. As a result, the measured inelastic neutron scattering spectra represent intrinsic motion of DNA molecules.

3. Results and discussion

Neutron scattering spectra measured for three samples at different temperatures are shown in Figure 1. The data are presented as imaginary part of the susceptibility spectra, $\chi''(q,\nu) = S(q,\nu)/n(\nu)$. The susceptibility presentation of neutron or light scattering data makes them directly comparable to dielectric $\epsilon''(\nu)$ or mechanical loss modulus $G''(\nu)$. It is well justified theoretically and is used very actively now in the field of dynamics of glass forming systems and polymers [13–18]. The susceptibility presentation has a few advantages in comparison with traditionally used dynamic structure factor $S(q,\nu)$: (i) trivial temperature variation, the Bose
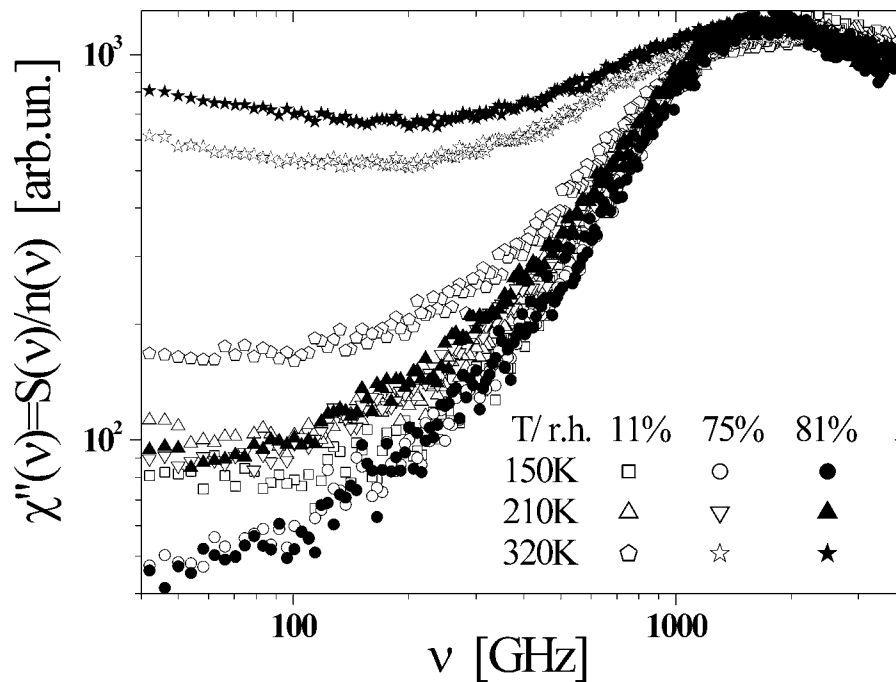
Figure 1. Neutron scattering susceptibility spectra of Li-DNA/D_2O samples at different levels of hydration measured with incoming neutrons $\lambda = 5$Å. The spectra present sum over all detectors and correspond to average $Q \sim 2$ Å^{-1}.

temperature factor $n(\nu) = [\exp(h\nu/kT)-1]^{-1}$, is taken into account; that represents a 'detailed balance' valid for all excitations in thermal equilibrium; harmonic excitations should demonstrate no temperature dependence in the susceptibility; (ii) relaxation process in the susceptibility spectrum appears as a maximum at $\nu_m \sim (2\pi\tau)^{-1}$, where τ is a characteristic relaxation time, a few relaxation processes with well separated τ will appear as a few separated peaks; (iii) single exponential relaxation will have spectrum $\chi''(\nu) \propto 2\pi\nu\tau/[1+(2\pi\nu\tau)^2]$, i.e. it has high- and low-frequency tails $\chi''(\nu) \propto \nu^b$ with b = –1 and +1, respectively. In the case of non-exponential (stretched) relaxation typical for complex systems, the tails will have power law with the exponent |b| < 1. Thus, the susceptibility presentation simplifies analysis of complex relaxation spectra.

Traditionally, quasielastic neutron or light scattering spectra of biomolecules are analyzed by a sum of a few Lorentzians. However, the susceptibility spectra presented in Fig.1 clearly show two well separated processes, both have strong stretching. Approximation of such complicated spectra by a Lorentzian (or by a sum of two or three Lorentzians) might give misleading results. It was shown in [19] that fit of the quasielastic neutron scattering spectra of a protein by Lorentzians gives parameters that depend on resolution function of the spectrometer and
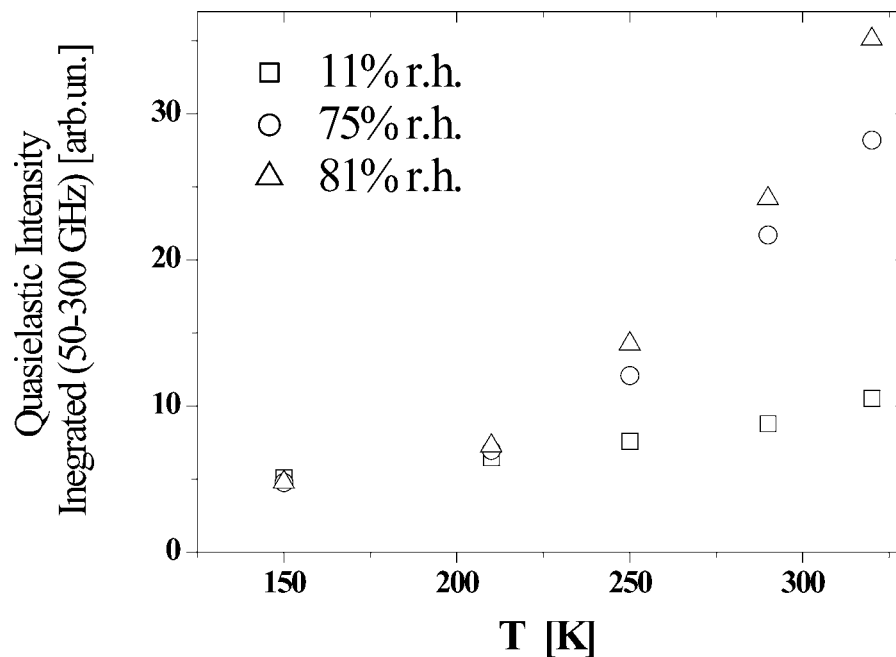
Figure 2. Relaxation contribution integrated in the frequency range 50–300 GHz for the samples with different levels of hydration.

frequency range chosen for the fit. That is the reason why we propose to analyze the neutron scattering spectra in the susceptibility presentation.

The spectra presented in Figure 1 show harmonic behavior (i.e. are temperature independent) at frequencies above ~1.5–2 THz. Vibrational excitations dominate this frequency range. Relaxation contribution dominates the spectra at frequencies below ~100–300 GHz and shows strong dependence on temperature and humidity. Figure 2 presents temperature dependence for the relaxation contribution integrated in the range 50GHz–300GHz. The data (Figures 1, 2) shows that all 3 samples demonstrate strong anharmonicity. Temperature variation of the relaxation intensity shows sharp rise at T above 210K in the samples with high water content. This is the well-known dynamic transition that appears to be suppressed in the dry sample. These data are consistent with observations of the dynamic transition in proteins [4–6].

It is interesting to note that at low temperatures the relaxation contribution (intensity below ~100 GHz) is stronger in the dry sample than in the wet samples. The result can be interpreted as higher flexibility of the dry DNA at lower temperatures. The water of hydration blocks intrinsic motion of DNA at low temperatures. The spectra of all 3 samples appear to be rather similar at T = 210K. At higher temperatures, however, the relaxation contribution increases strongly with increase in water content (Figures 1, 2). That can be interpreted as an increase in flexibility due to softening DNA molecule by water of hydration at high temperatures. Thus

the data demonstrate two opposite influences of hydration on dynamics of DNA: At low temperatures (below $\sim$210K) the water of hydration makes the DNA molecule stiffer, suppresses conformational jumps, while at higher temperatures (T above $\sim$210K) water of hydration makes DNA molecule softer and enables more intense conformational motion.

Figure 3 presents the spectra of the same samples obtained with higher energy resolution. The spectra show that two relaxation processes are present in DNA: the fast process that dominates at $\nu >$200 GHz and the slow process that dominates at $\nu <$100 GHz. The maximum of the slow process is out of the frequency range, i.e. $\nu_m <$10 GHz. That corresponds to characteristic relaxation time longer than $\sim$0.01 ns. High frequency tail of the slow process has power-law spectral shape, $\chi''_{slow}(\nu) \propto \nu^{-b}$, with apparent b$\sim$0.25 independent on T and humidity. The value of the exponent b is consistent with our previous results obtained for another DNA/D_2O sample on another spectrometer (MIBEMOL, Saclay, France) [20]. For a single exponential relaxation the exponent b = 1 and $\chi''(\nu) \propto \nu^{-1}$. Thus the observed low value of the exponent b indicates strong stretching of the slow process. Strong stretching is typical for polymeric systems and is usually interpreted either as a broad distribution of relaxation times or as a complex relaxation process.

Figure 4 presents back-scattering data that extend our frequency range to lower ν. No variations is observed for the wet sample spectra between T$\sim$5K and T$\sim$210K. The slow process shows up at T$\sim$250K and is much stronger at T$\sim$315K. No difference in the back-scattering spectra measured at T$\sim$210K and at T$\sim$315K can be detected for the dry sample.

The results (Figures 3, 4) show that the slow process depends strongly on temperature and humidity. It doesn't appear in the dry sample even at the highest temperature of our measurements, T = 320K, and disappear from our frequency window in the wet samples at T below $\sim$210K (Figures 3, 4). Thus from the point of view of dynamics, the decrease in humidity is similar to decrease in temperature. That statement is correct for high (above 210K) temperatures only. Around T$\sim$210K the spectra of all samples look similar. Thus it seems that the influence of humidity and temperature is similar for the slow process only.

Comparison of the data presented in Figure 2 and in Figures 3, 4 suggests that the dynamic transition usually observed in hydrated bio-polymers at $T_d \sim$200–230K is related to the slow process. Strong rise of the quasielastic intensity at temperatures above T_d (Figure 2) correlates with appearance of the slow relaxation process (Figures 3, 4). Thus the observed sharp increase of the mean-squared displacements $<x^2>$ for hydrated bio-polymers may be related to the slow relaxation process.

The nature of the slow process is not known. It was observed in neutron scattering spectra, but also in dielectric and NMR relaxation data [21–23]. The dielectric data for hydrated DNA identified a relaxation process with characteristic relaxation time $\tau \sim$1 ns ($\nu_m = (2\pi\tau)^{-1} \sim$100 MHz) at T$\sim$300K [21]. The authors ascribed this process to relaxation of water molecules bounded to a bio-polymer surface
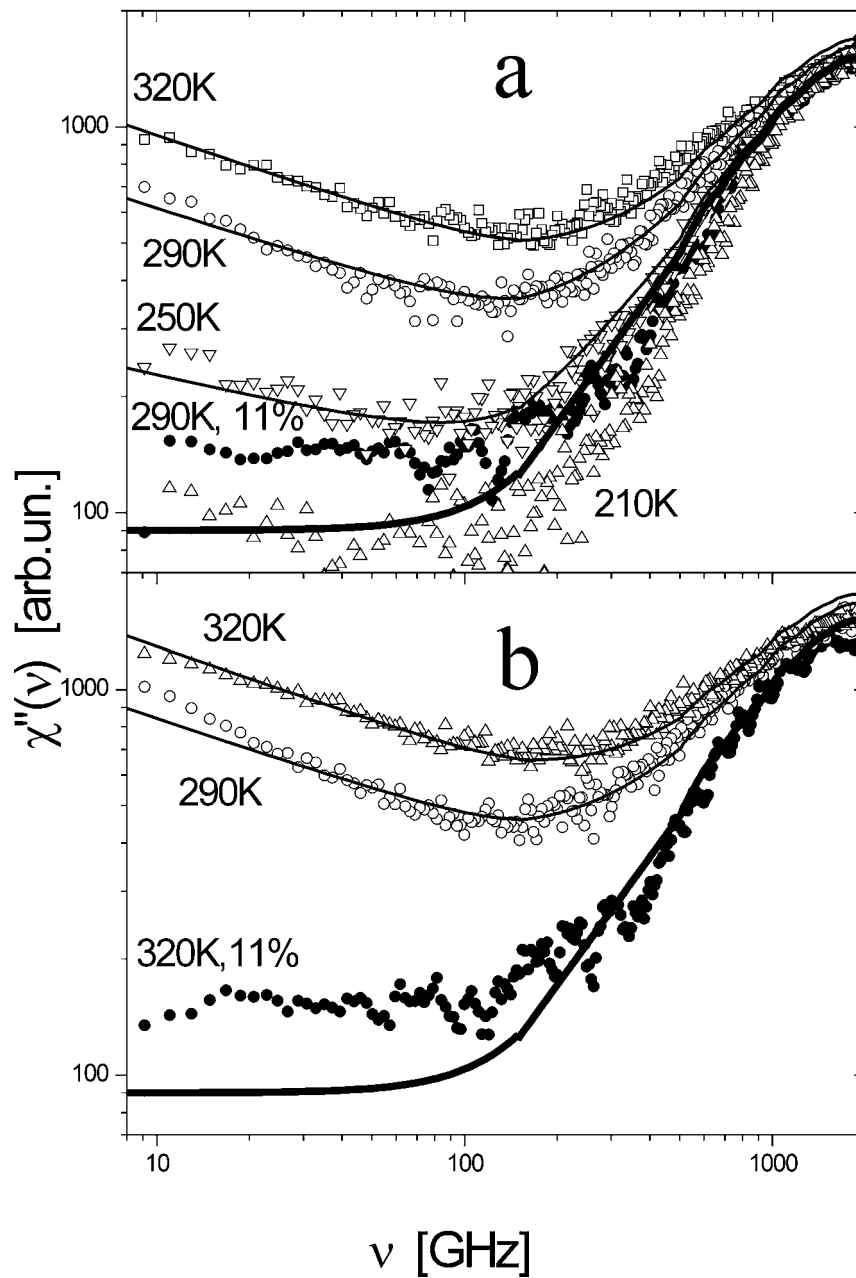
Figure 3. Neutron scattering spectra measured with $\lambda = 8\text{Å}$ for the sample hydrated to 75% r.h. (a) and to 81% r.h. (b). The spectra present sum over all detectors and corresponds to average $Q \sim 1.8 \text{ Å}^{-1}$. The open symbols are experimental data; the thin solid lines are results of the fit using eq.3; the thick solid line is the spectrum of the fast dynamics, $\chi''_{fast}(\nu)$; the closed circles is the spectrum of the dry sample. Temperatures are shown by numbers.
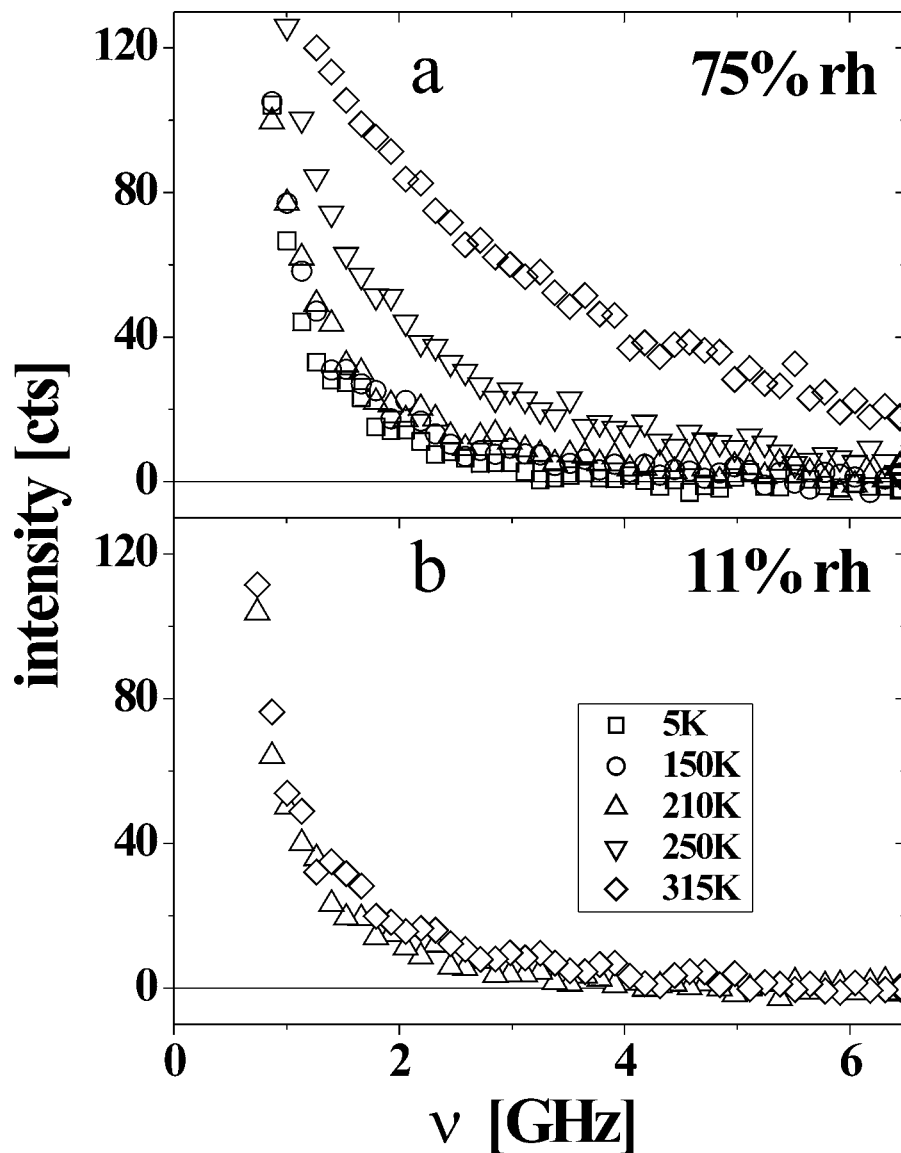
Figure 4. Neutron scattering spectra measured with λ = 6.37Å at the Back-scattering spectrometer for the wet (top) and the dry (bottom) samples at different temperatures.

[21]. They suggested a model that assumes jumps of water molecules between two positions. The model is based on the fact that the dielectric response of hydrated bio-polymers is dominated by the water because water molecules have strong dipole moment. However, analysis of ^{13}C-, ^{31}P- and H- NMR of hydrated DNA also demonstrate relaxation process with $\tau \sim$1–2 ns at T$\sim$295K [22, 23]. This process
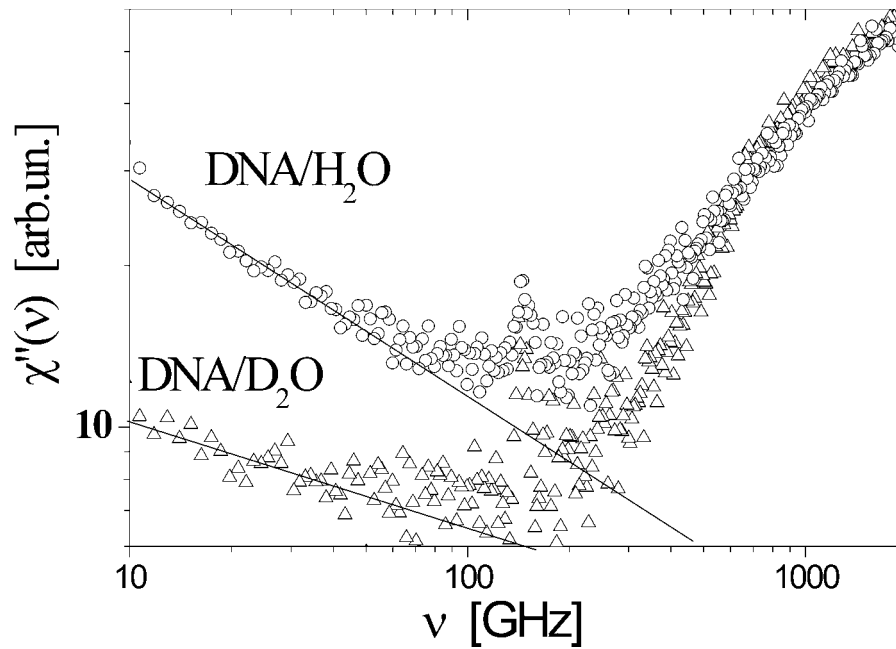
Figure 5. Comparison of neutron spectra of Li-DNA samples hydrated to 75% r.h. with D_2O and H_2O. The spectra were measured at T = 293K with neutrons λ = 9Å and normalized to number of hydrogen atoms [11]. The solid lines show the apparent slope of the tail of the slow process, b∼0.2–0.25 for the sample hydrated with D_2O and ∼0.35–0.4 for the sample hydrated with H_2O.

certainly can not be ascribed to motion of water molecules and was interpreted as a coupled motion of deoxyribose sugars and the sugar-phosphate backbones.

The presented neutron scattering spectra (Figures 3, 4) are dominated by contribution of hydrogen atoms of DNA. Contribution of D_2O is negligible due to large difference in scattering cross-section of H and D atoms. Thus our results support the conclusion of the NMR data analysis: the slow relaxation process is intrinsic motion of the DNA molecule. Additional argument in favor of this conclusion comes from analysis of the spectra of DNA hydrated with D_2O and H_2O. These data were obtained earlier on the MIBEMOL time-of-flight spectrometer in Saclay and were published in [11]. Comparison of the spectra is presented in Figure 5. Li-DNA samples hydrated to 75% r.h. with H_2O have approximately 15 H_2O molecules per base pair of DNA. That gives ratio of number of hydrogen atoms in DNA and in hydration shells $H_{DNA}:H_{water}$∼3:4. Thus the contribution of water molecules to the neutron scattering spectrum of DNA/H_2O sample (Figure 5) is around 60% and should be seen. The spectra of the two samples are clearly different in the region of the slow process: the slow process contribution is more intense and has smaller stretching (the exponent b is nearly twice large in DNA/H_2O sample than in DNA/D_2O sample). Thus, relaxation motion in water molecules of hydration has spectral shape of the slow process with the stretching parameter different from
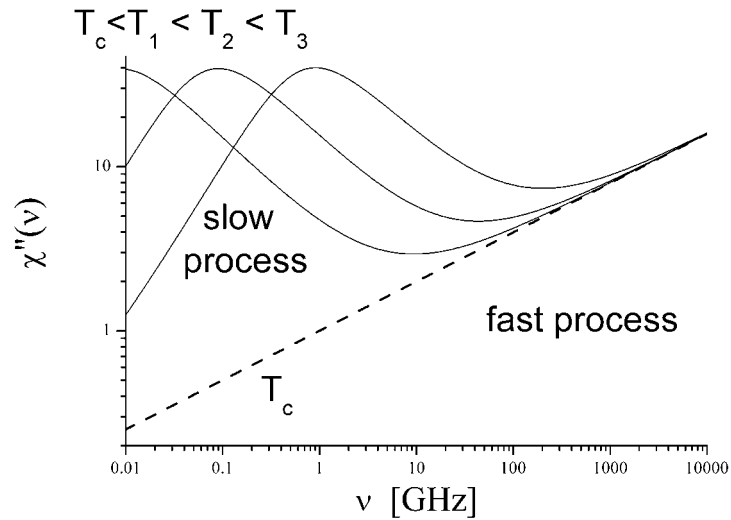
$$T_c < T_1 < T_2 < T_3$$

Figure 6. Sketch of the MCT predictions for the susceptibility spectrum at temperatures above T_c. The fast dynamics is essentially temperature independent. The main variations are the shift of the slow process to lower frequencies with temperature decrease. The dashed line shows the spectrum expected in idealized version of MCT at T_c.

DNA/D$_2$O system. It is closer to the stretching parameter observed for bulk water, b~0.65 [24]. This result (Figure 5) gives additional evidence in favor of the idea that the slow process observed for DNA/D$_2$O samples reflects intrinsic motion of DNA molecule.

In our recent work [20] we suggest that neutron scattering spectra of DNA can be described using ideas of mode-coupling theory (MCT) [13]. MCT was suggested for description of the glass transition and predicts particular scenario for relaxation in glass-forming liquids. For details of the theory one can be addressed to review articles [13]. The theory predicts that at high temperatures the relaxation process should occur in two steps: first, at very short time scale, system can relax to some certain level only, then, at much longer time scale, complete relaxation occurs through a second step. Both relaxation steps are not single exponential decays, they are strongly stretched. MCT predictions for the susceptibility function are shown schematically in Figure 6. The susceptibility should demonstrate a minimum between fast and slow processes and can be approximated by a sum of two power laws:

$$\chi''(\nu) = \chi''_{slow}(\nu) + \chi''_{fast}(\nu) = A_{slow}[\nu\tau_\alpha]^{-b} + A_{fast}\nu^a \qquad (1)$$

Here A_{slow} and A_{fast} are amplitudes of the slow and the fast process, respectively, τ_α is relaxation time of the slow process; the exponents a and b are interrelated through a transcendent equation [13]. According to the MCT scenario at high temperatures (Figure 6), the spectrum of the fast process is essentially temperature independent, the only parameter that demonstrates significant temperature variation is τ_α. It should have critical temperature behavior:

$$\tau_\alpha(T) \propto (T - T_c)^{-\gamma} \text{ with } \gamma = \frac{1}{2a} + \frac{1}{2b} \tag{2}$$

Thus all 3 critical exponents, a, b and γ, are interrelated. The theory predicts a dynamic transition at T_c where relaxation behavior should change qualitatively.

Many experimental works [13] and computer simulations [13, 14] demonstrated reasonable agreement with the qualitative MCT scenario (Figure 6) at temperatures above T_c. It was also found that the spectrum of the fast dynamics does not follow the asymptotic prediction (eq. 1), presumably due to strong interference with the vibrational contribution [15,16]. Comparisons of the theory with experiments and simulations have been done also for synthetic polymers [14, 17, 18] and reasonable agreement has been found.

The microscopic picture behind the high temperature MCT scenario (Figure 6) for polymer melts can be described as follows. The fast process presents some kinds of rattling of segments in a cage formed by their neighbors, i.e. it is local conformational jumps between few different configurations. This process occurs at picosecond time scale, it has weak temperature dependence and leads to a partial relaxation only. At longer times, the cage can relax due to motion of neighbor segments. That leads to complete (global) relaxation. The fast process is a necessary precursor of the slow process.

Analysis of DNA spectra (Figure 3) immediately reveals good qualitative agreement with the asymptotic MCT scenario (Figure 6): There is the two-step scenario, both steps have stretched (non-exponential) spectral shapes, the main variation of the spectra is the shift of the slow process to lower frequencies with decrease in temperature. For more quantitative analysis we did a fit of the DNA spectra using modified eq. 1:

$$\chi''(v) = A_{slow}[v\tau_\alpha(T)]^{-b} + \chi''_{fast}(v) \tag{3}$$

where we dropped relation between the exponents a and b, because it usually does not hold [15–18]. To fit the data at all temperatures and humidity levels we used only one free parameter $\tau_\alpha(T)$. The spectrum $\chi''_{fast}(v)$ and the exponent b were chosen using iteration procedure described in [20] and fixed. All other parameters were kept constant. The best fit was achieved with the spectrum $\chi''_{fast}(v)$, shown in Figure 3, and the exponent b = 0.3, slightly higher than the apparent slope of the tail of the slow process. The results of the fit are presented in Figure 3 and give good description of the experimental data. It is important to note that we were
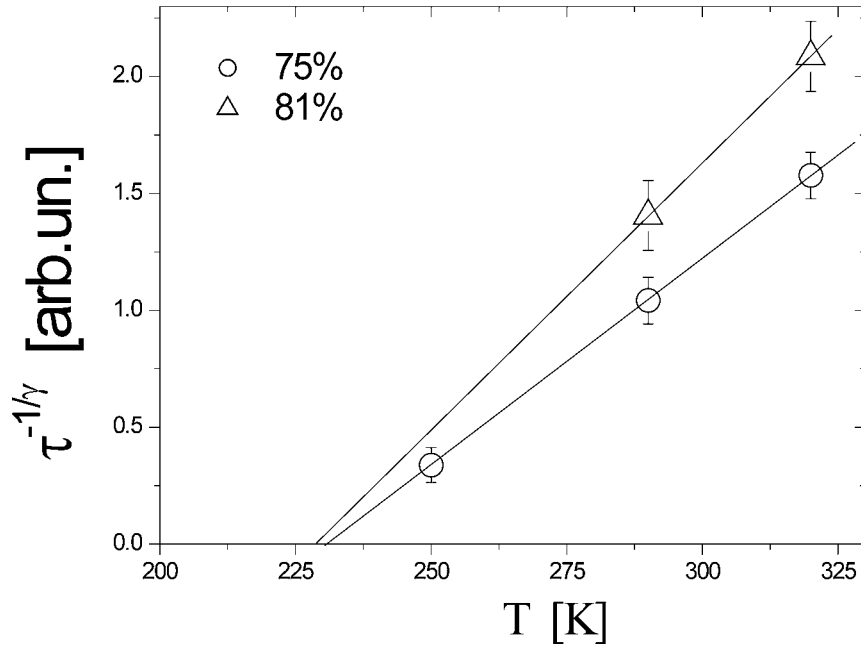
Figure 7. Temperature dependence of the only free fit parameter τ_α (eq.3). Estimates give $T_c \sim 230K$ for both samples in agreement with [20] and with T_c of bulk water [24].

able to fit the spectra of both wet samples with the same $\chi''_{\text{fast}}(\nu)$ and b. Moreover, $\chi''_{\text{fast}}(\nu)$ is similar to the spectrum of the dry sample at high temperatures. Thus the fast relaxation spectrum at high temperatures seems to be only slightly dependent on the level of humidity.

As a cross-test of the results of the fit, we analyzed temperature dependence of the only free fit parameter, $\tau_\alpha(T)$, using equation 2 (Figure 7). The exponent γ was fixed through its relation to the exponent b, $\gamma = 3.9$ for b = 0.3 [13]. Unfortunately, the number of temperature points in our experiment is very limited. Nevertheless, $\tau_\alpha(T)$ for these few points demonstrates expected (eq. 2) temperature behavior and gives $T_c \sim 230K$ in wet samples independent (with our accuracy) on level of humidity. It is important to note that the so-obtained T_c is similar to previous estimates obtained from analysis of another DNA sample measured on another spectrometer [20]. These results confirm that MCT can consistently describe the neutron scattering data of hydrated DNA and that the dynamic transition observed at $T \sim 200–230K$ can be ascribed to the predicted by MCT crossover from liquid-like to solid-like behavior in dynamics.

This analysis gives us additional hint for understanding of the slow process in DNA. Following the MCT interpretation, it corresponds to global relaxation of segments, i.e. base-pairs and backbones of DNA molecule. It should be cooperative process involving many segments. That interpretation is consistent with analysis of

NMR relaxation data. In particular, authors of [23] interpret H-NMR spectra as an evidence of large amplitude motion of base planes. They proposed a model that relates nanosecond relaxation to worm-like motion of the helix itself, rather than a fluctuation of nucleotide geometry inside the helix.

Thus the slow process is intrinsic relaxation process of DNA molecule. The microscopic picture behind the slow and the fast relaxation processes in DNA is not clear and the presented data do not provide sufficient information. We can, however, suggest some speculations. Following the MCT ideas, we can interpret the fast picosecond process as a rattling of segments (nucleotides) in a cage formed by their surrounding, other nucleotides and water molecules. This motion presents local conformational jumps of a small part of the whole molecule and provides only partial relaxation. That means that the molecule remains non-ergodic on a time scale shorter than the slow process (relaxation of the cage). Similarity of the fast dynamics spectra in the samples with different hydration levels (Figure 3) suggests that the local relaxation of segments is similar in dry and wet samples at high temperatures. However, when water is frozen, the motion of nucleotide in the cage becomes more restricted and that leads to lower amplitude of the fast process in the wet samples at T below ~200K (Figure 1).

At higher temperatures, the global relaxation of DNA becomes active in the wet samples. This slow process leads to a sharp rise of the mean-squared atomic displacement $<x^2>$ and thus can be considered as the reason for the dynamic transition. The slow process allows global relaxation of a polymer and the system becomes ergodic. It means that the system can visit all conformational states in a reasonable time. We speculate that this is the mechanism for enabling functions of bio-molecules. In the dry state, the bio-polymer remains stiff, the cage does not relax on a reasonable time scale even at highest temperature.

4. Conclusions

Analysis of neutron scattering data of Li-DNA/D_2O samples shows that dynamic transition observed in hydrated bio-polymers at T~200–230K is related to appearance of a slow relaxation process in GHz frequency range. The dynamic transition is usually observed as a sharp rise of mean-squared atomic displacements at this temperature range and was ascribed to strong rise of anharmonicity in molecular motion. Our observations demonstrate that the rise in $<x^2>$ is related to particular relaxation process (the slow process) rather than to general anharmonicity. The slow process varies strongly with temperature and humidity and is suppressed in the dry sample.

The nature of the slow process remains unclear. Experimental data suggests that this is intrinsic relaxation process of DNA. We ascribe it to global relaxation of the molecule similar to primary segmental relaxation in synthetic polymers. The conclusion agrees with earlier assignment of nanosecond relaxation in DNA based on analysis of NMR data [22, 23]. It is shown that the relaxation spectra

at temperatures above the dynamic transition can be described by mode-coupling theory [13]. In that case, the observed dynamic transition can be related to the dynamic transition suggested by MCT for the description of the glass transition phenomenon. It corresponds to transition of dynamics on a molecular level from a liquid-like to a solid-like behavior. In the case of solid-like dynamics, molecular motion is restricted by frozen (on a molecular time scale) surroundings.

In that interpretation, molecules in the dry sample are still moving like in a solid systems and only addition of water enables large scale motion. This might be the reason why decrease in water of hydration is similar to decrease in temperature from the point of view of dynamics. All these data support our previous speculation [20] that the dynamic transition is driven by the water of hydration. Bulk water has the dynamic transition at temperatures T∼220–230K [24]. Data with better energy resolution are required to check temperature and humidity dependence of the slow process, its relaxation time and relation to the dynamic transition. It remains a challenge to understand how general our observations on DNA are for other bio-polymers.

Acknowledgements

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