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Abstract.   Single crystals of the orientational glass $(KI)_{0.56}(NH_4I)_{0.44}$ have been studied using iodine NMR for temperatures 1.8 K $< T <$ 300 K. Two-dimensional spectroscopy has shown that the quadrupole-perturbed central transitions are predominantly inhomogeneously broadened. The orientational glass transition is already accompanied by a considerable increase of that broadening in the regime of fast motion. Evidence for a random-field smearing of the random-bond-induced freezing process is obtained. Measurements of the spin–lattice relaxation time reveal the existence of a broad distribution of orientational correlation times at low temperatures.

1. Introduction

Orientational glasses (OGs) are crystalline materials in which aspherical molecular units or pseudo-spins freeze into a disordered low temperature state. This state bears a number of similarities to the amorphous phase of conventional glass-forming materials which is still not fully understood [1]. The relative structural simplicity of OGs has stimulated numerous theoretical studies aiming at enhancing the understanding of the nature of the freezing process in these materials [2, 3]. What makes the OGs particularly attractive is the fact that, analogous to the case of magnetic spin glasses, an Edwards–Anderson order parameter q_{EA} can be defined. Hence the influence of static random fields, which are usually a prominent feature of OGs can be studied in detail. In some cases these effects seem to dominate the orientational freezing process while in other cases they have been reported to be rather weak.

The solid solutions of potassium and ammonium iodide seem to belong to the latter, less complicated class of materials. These crystals exhibit a pseudo-cubic structure at room temperature. Here the NH_4 group is slightly distorted, leading to the occurrence of a relatively large dipolar moment causing anisotropic interactions [4]. Above a critical NH_4 concentration $x > 0.55$ the crystals undergo structural phase transitions accompanied by various long-range orientationally ordered states of the molecular ions. For $x < 0.2$ the interactions among the tetrahedrally shaped ammonium groups are relatively weak and a single-ion type of slowing down results.

The glass transition and the glassy low-temperature state which is obtained in $(KI)_{1-x}(NH_4I)_x$ for $0.2 < x < 0.6$ are currently being studied intensively using various experimental techniques including Raman [5], x-ray [6] and neutron scattering [7, 8], dielectric spectroscopy [4, 8, 9], and nuclear magnetic resonance (NMR). As probe nuclei in the NMR studies the deuteron ^2H [10] and the nitrogen isotope ^{14}N [11] have been

used. These nuclei probe the orientational degree of freedom most directly. However also the nuclei located on orientationally fixed sites of the lattice, viz. iodine and potassium, are suited for NMR studies. In particular the ^{127}I species, which is characterized by an extraordinarily large quadrupole moment, can serve as a sensitive probe for an investigation of the OG transition. Iodine NMR is additionally attractive due to the fact that upon lowering the temperature the NH_4 group freezes into the C_{3v} orientation [12]. In this symmetry three out of the four protons closely approach the adjacent iodine ions while the fourth proton points along the body diagonal direction of the cubic cell. Hence the electric field gradients (EFGs) at the iodine site should depend on whether a proton comes very close to the probe nucleus or not. Due to the local nature of the dominant quadrupolar interaction a splitting of its absorption spectrum should be observable provided the protonic motion freezes out completely. At higher temperatures fluctuating EFGs at the iodine site associated with reorientational motions of the ammonium group are expected to permit further insights into the freezing process.

The remainder of this paper is organized as follows. After giving some experimental details, in section 3 we present the orientation and temperature dependence of the NMR line shape as well as the temperature dependence of the spin–lattice relaxation times. Then we discuss the significance of the temperature-dependent line widths and finally summarize our findings.

2. Experimental details

For the present study we have used a previously investigated single crystal with an ammonium concentration $x \approx 0.44$. Measurements of spectra and spin–lattice relaxation times were carried out at a Larmor frequency of $\nu_L = 76.056$ MHz. The length of a 90° pulse was usually 4.1 μs. Using a ^{4}He-flow cryostat temperatures between 1.8 and 300 K could be achieved and maintained stable to within ±0.2 K.

3. Results and analyses

3.1. Orientation and temperature dependent spectra

A set of representative spectra taken at room temperature is shown in figure 1 for various orientations. They are associated with the central $1/2 \rightarrow -1/2$ transition in the quadrupolar perturbed spectra of the iodine nucleus which carries a nuclear spin of $I = 5/2$ and a relatively large quadrupole moment of $eQ = -0.785 \times 10^{-24}$ cm^2. Due to the combined effects of second-order quadrupole shifts and a broad distribution of EFGs the lines exhibit asymmetric shapes and relatively large halfwidths.

It is clear however that also a distribution of chemical shifts contributes to the spectral broadening. In order to allow for an estimate for the relative importance of these effects it is noted that the ^{127}I resonance in pure KI and pure NH_4I exhibit chemical shifts that are separated by about 9.2 kHz. The peak of the room-temperature spectrum taken for $(KI)_{0.56}(NH_4I)_{0.44}$ at 0° is located in between those of the pure compounds and is 8 kHz from the iodine resonance of KI. This large frequency shift and consequently frequency distribution that naturally arises in mixed crystals is ascribed to the extraordinarily large polarizability of the electronic shell of ^{127}I.

In figure 2 we present the first moment (with respect to ν_L) and second moment, denoted as M_1 and M_2, respectively, of the spectra shown in figure 1. Both components exhibit the angular dependence expected for crystals with a structure which is cubic on average. Using
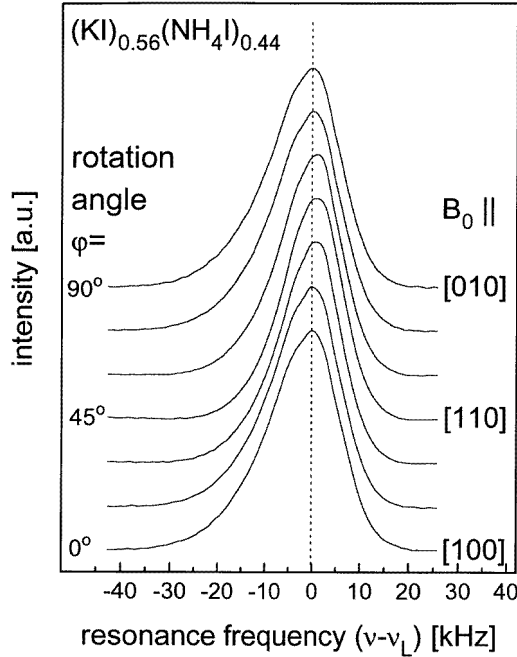
Figure 1. Spin echo spectra of the central transition of the ^{127}I resonance in (KI)$_{0.56}$(NH$_4$I)$_{0.44}$ taken at room temperature. The crystal was oriented with one cubic axis along the direction of the external magnetic field and then rotated by several azimuthal angles φ. The dashed line corresponds to $\nu_L = 76.056$ MHz.

second-order perturbation theory Wiotte *et al* have shown that in such crystals M_1 should obey the relationship [13]

$$M_1(\varphi) = \left(K^2/4\nu_L\right)\left\{\tfrac{1}{4}\left[V_{aa}^2\right]\left[1 - \tfrac{9}{4}\sin^2(2\varphi)\right] + \left[V_{ab}^2\right]\left[\tfrac{3}{4}\sin^2(2\varphi) - 1\right]\right\}. \tag{1}$$

Here $K = eQ/h$ is proportional to the quadrupole moment and φ is the azimuthal angle. $[V_{aa}^2]$ as well as $[V_{ab}^2]$ denote the ensemble averages (i.e. averages over the local disorder) of the only two non-vanishing, independent second moments of the distribution of EFGs and hence are a measure of the local deviations from the mean cubic symmetry of the crystals.

From the rotation pattern shown in figure 2(a) we obtain $[V_{ab}^2]/[V_{aa}^2] \approx 3$, which should be considered as an approximation due to the extreme sensitivity of the ratio to the fit parameters. This relative large magnitude of the off-diagonal contribution indicates major deviation of the principal axes of the local EFG tensors from the cubic crystalline axes. These deviations are not unexpected since the C_{3v} orientation of the ammonium protons, which presumably dominates the contributions to the EFG at the iodine site, is incompatible with the average cubic symmetry of the crystal lattice.

The theoretical calculation of the associated second moments is relatively complicated and in addition to the averages appearing in equation (1) involves the terms $[V_{aa}^4]$, $[V_{ab}^4]$, and $[V_{aa}^2 V_{bb}^2]$. Since these coefficients cannot be determined independently from the present data we prefer to describe them empirically by $M_2 = M_0 + A \sin 4\varphi$. The angular dependence of M_2 apart from second-order shifts can be ascribed to the φ-dependent asymmetry of the spectra. We find $M_0 = 60.7$ kHz^2 and $A = 13.9$ kHz^2.

In the following we will focus on the temperature dependence of the ^{127}I central lines
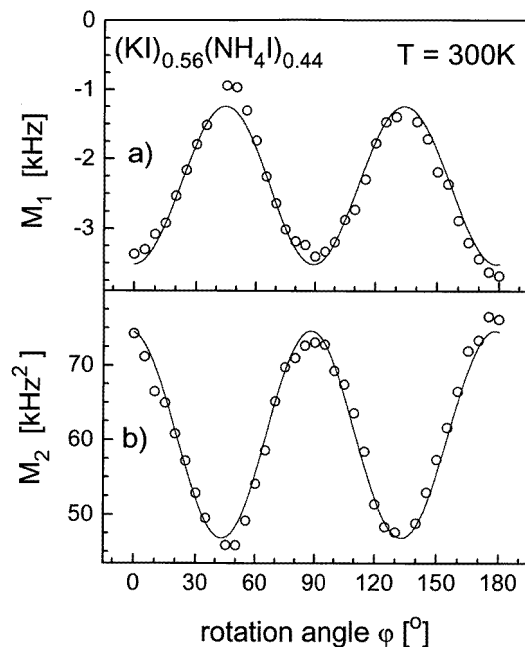
Figure 2. The angular dependence of first and second moments of the spectra shown in figure 1. The solid line in the upper panel has been calculated using (1). The solid line in the lower panel has been calculated using the empirical expression $M_2 = M_0 + A \sin 4\varphi$ and the parameters given in the text.

as measured with one of the cubic axes oriented along the magnetic field (see figure 3). It is evident that for temperatures $T > 100$ K the half widths change only slightly but increase considerably on further cooling. It should be noted that this broadening of the lines is *not* accompanied by any appreciable changes in their general shape.

In order to elucidate the origin of the line broadening we have carried out two-dimensional separation of interaction measurements as described in detail elsewhere [14]. From the two frequency axes as shown in figure 4 the homogeneous and the inhomogeneous contributions to the line broadening seen in the 1D spectra can be read off from the ordinate (ν_1) and abscissa (ν_2) axes, respectively. One obtains dipolar line widths smaller than $\Delta \nu_1 = 2.7$ kHz for all temperatures at which 2D spectra were taken and hence the inhomogeneous broadening dominates. Inhomogeneously broadened spectra which widen upon lowering the temperature are a well known feature of orientational glasses and will be discussed in section 4, below.

3.2. Spin–lattice relaxation

The longitudinal magnetization recovery $M(t)$ was measured using a $180°–t–90°$ sequence. $M(t)$ was non-exponential as expected for nuclei with $I > 1$. This precluded a simple analysis as carried out previously for deuteron and nitrogen nuclei [10, 11]. From the experimental $M(t)$ data effective spin–lattice relaxation times $\langle T_1 \rangle$ were calculated using the empirical Kohlrausch function $M(t) \propto \exp[-(t/T_1)^\beta]$. Employing the gamma function one finds $\langle T_1 \rangle = T_1 \Gamma(1/\beta)/\beta$. Typically the stretching parameter was $\beta = 0.8 \pm 0.2$.

The temperature dependence of $\langle T_1 \rangle$ is shown in figure 5. From the pronounced
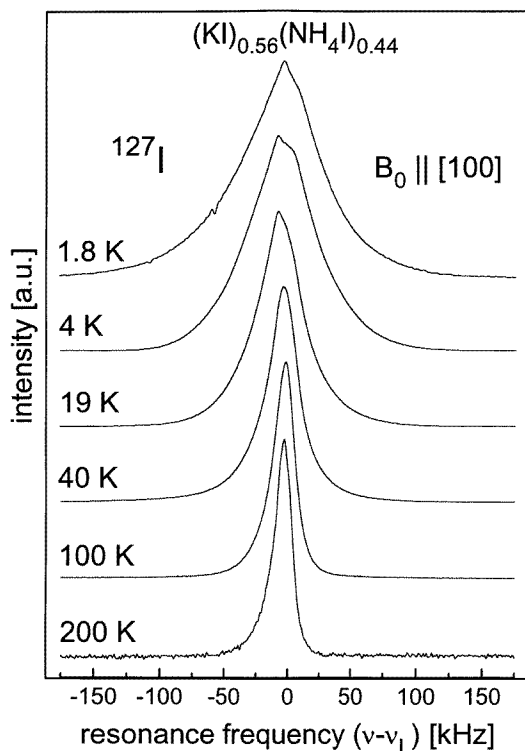
Figure 3. Temperature-dependent ^{127}I absorption spectra of (KI)$_{0.56}$(NH$_4$I)$_{0.44}$. Note that the width of the spectra changes only slightly for temperatures above about 100 K, but below this temperature the absorption lines exhibit a pronounced broadening.

asymmetry of the T_1–$1/T$ curve it is evident that spin–lattice relaxation in (KI)$_{0.56}$(NH$_4$I)$_{0.44}$ is not of the simple BPP type [15], but rather indicative of a distribution of correlation times τ_c. However, for temperatures far above the T_1 minimum, i.e. in the fast-motion regime, $2\pi\nu_L\tau_c \ll 1$, the spin–lattice relaxation is proportional to $1/\tau_c$. The solid line in figure 5 therefore implies Arrhenius behaviour $\log \tau_c \propto E/T$. The effective hindering barrier estimated from our data is $E = 5.5$ meV. This value is compatible to that previously obtained with ^{14}N-NMR on the same crystal [11]. It is interesting to note that in a deuterated crystal of about the same ammonium concentration the energy barrier was found to be about twice the size [10]. At very low temperatures ($T \approx 2.2$ K) the spin–lattice relaxation times exhibit a shoulder which could be interpreted as signalling the slowing down of motion associated with the ammonium ions. It should be noted that no significant change of the lineshape is found at these low temperatures, which precludes a more detailed interpretation of the shoulder.

4. Discussion

The temperature dependence of the spin–lattice relaxation times as well as that of the spectra show that the iodine nucleus is a useful probe of the reorientational dynamics of the ammonium ions, which are thought to drive the freezing process. In most orientational glasses not only does the direct coupling of the orientational degrees of freedom (random
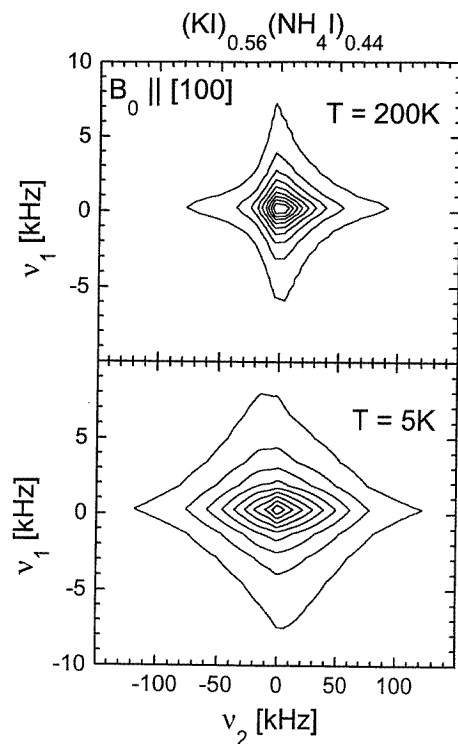
Figure 4. Contour plots of two-dimensional 'separation of interactions' spectra taken at $T = 200$ K and $T = 5$ K. Along the ν_1 and ν_2 axes the homogeneous and inhomogeneous broadening respectively shows up.
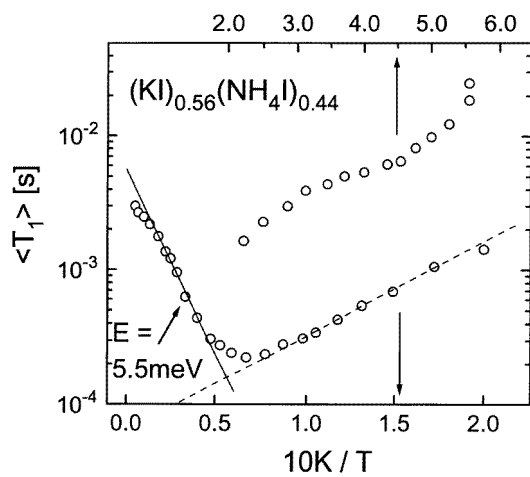

Figure 5. Effective spin–lattice relaxation times $\langle T_1 \rangle$ of a single crystal of $(KI)_{0.56}(NH_4I)_{0.44}$ plotted as a function of inverse temperature. The solid and dashed lines represent Arrhenius expressions with energy barriers of 5.5 and 1.4 meV, respectively.

bonds) play an important role, but also their coupling to the static disorder (e.g. local strains) present in the crystal lattice. Previous studies of (KI)$_{0.56}$(NH$_4$I)$_{0.44}$ have indicated that the strength of these so-called random fields is small as compared to that of the random bonds [10, 11]. In contrast to the nitrogen and deuteron nuclei, the iodine probe is located directly on the static lattice and owing to its very large quadrupole moment it may be expected that ^{127}I is particularly sensitive to local deviations from the overall cubic symmetry.

At high temperature these deviations can be anticipated to be averaged out to a large extent due to the rapid reorientations of the ammonium groups. The freeze-out of the motion of molecular ions is therefore expected to lead to variations in the NMR line shape. This expectation is nicely confirmed by the results shown in figure 3 where it can be seen that the absorption lines broaden considerably, i.e. their half widths $\Delta \nu_H$ increase, but only for temperatures below about 50 K. The spread in the local resonance frequencies $\Delta \nu$ in OGs can thus be attributed to the freezing of the orientational degrees of freedom or, in other terms, to an increase of the local polarization p. It should be noted that at low temperatures no splitting of the absorption spectrum is observed. Therefore no indication for a freeze-out of the NH$_4$ group into a particular C$_{3v}$ orientation is found.
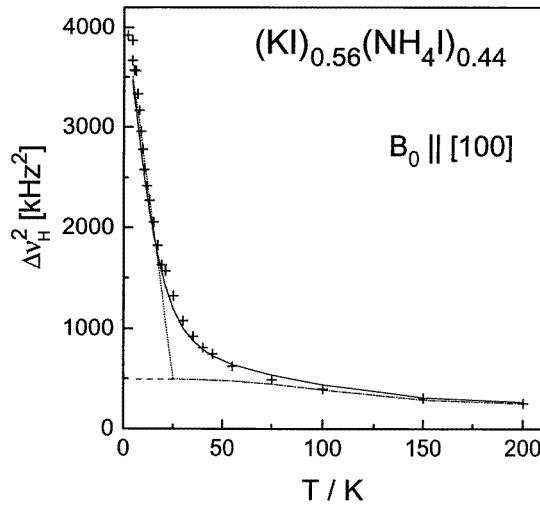

Figure 6. Squared halfwidths $\Delta \nu_H^2$ of the ^{127}I resonance as a function of temperature. The dashed line represents contributions due to thermal expansion as discussed in the text. The other lines are calculated using (3): solid line, $T_g = 15$ K, $T_\Delta = 12$ K; dotted line, $T_g = 25$ K, $T_\Delta = 0$ K.

Figure 6 summarizes the temperature dependence of the second moments estimated from the halfwidths of these absorption lines ($M_2 \propto \Delta \nu_H^2$), which exhibit an increase that is more than fourfold between room temperature and 4 K. For a number of OGs a linear relationship between the shift of the resonance frequency $\Delta \nu$ and the local polarization p has been found [16]. Under these circumstances the second moments M_2 of the NMR spectra are proportional to the Edwards–Anderson order parameter q_{EA} [3, 11, 13]. Assuming that the linear approximation $\Delta \nu \propto p$ also holds in our case $M_2(T)$ may be written as being made up by several contributions as follows:

$$M_2(T) = M_2(q_{EA}) + M_2(a) + M_{2,0}. \qquad (2)$$

Apart from the relevant term $M_2(q_{EA}) \propto q_{EA}$ the experimentally determined second moment

is affected by variations in the lattice constant a and by the (temperature independent) broadening due to local variations of the chemical shifts. The connection between M_2 and a arises because thermal contraction leads to an increase of the EFG at the site of the probe nucleus. We have estimated the contribution due to the thermal lattice expansion, as indicated by the dashed line in figure 6, on the basis of x-ray data reported by Umeki *et al* [6].

For the quantitative analysis of the Edwards–Anderson order parameter we have used a mean-field model which incorporates simultaneously random bonds and random fields. In three dimensions this model yields an expression that has to be solved self-consistently [3]

$$q_{EA} = \frac{1}{\sqrt{2\pi}} \int \mathrm{d}x \, \mathrm{e}^{-x^2/2} \tanh^2 \left[x \sqrt{q_{EA}(T_g/T)^2 + (T_\Delta/T)^2} \right]. \tag{3}$$

Here T_g and T_Δ are measures of the contributions due to random bonds and random fields, respectively. The best fit of (3) to the experimental data, as represented by the solid line in figure 6, yields $T_g = 15$ K and $T_\Delta = 12$ K. A description in terms of a pure random bond *ansatz* (dotted line in figure 6, $T_g = 25$ K and $T_\Delta = 0$ K) which fits the data below about 20 K, is clearly inadequate at higher temperatures.

It is interesting to compare these findings with the results from previous NMR studies on $(KI)_{1-x}(NH_4I)_x$. In deuteron magnetization recovery experiments of $(KI)_{0.5}(ND_4I)_{0.5}$ the sharp onset of non-exponential T_1 relaxation near 40 K was interpreted to signal a dominance of random bond freezing [10]. A very similar behaviour of the magnetization recovery was also found in a ^{14}N-NMR investigation of $(KI)_{0.56}(NH_4I)_{0.44}$ [11]. However the width of the nitrogen resonance as measured on the same sample as in the present study has yielded a much lower T_g of 12.8 K. The seeming disparity between the two results may be resolved by noting that a recent calculation [11] has shown that non-exponential relaxation arises whenever the distribution of local polarizations is present in the system, irrespective of whether this is due to random bond or to random field effects. Furthermore the choice of different methods used to analyse the non-exponential relaxation can lead to different apparent smearings of the orientational glass transition [17].

However even the random field contributions to q_{EA} as extracted from the *line widths* of the ^{14}N and ^{127}I resonances are found to differ by a factor of three. Reassuringly however, the random bond contributions from both experiments agree within experimental error. This finding suggests that the iodine probe with its enormously large electrical quadrupole moment is more sensitive to local strains than the nitrogen [11] and (to a much larger extent) the deuteron [10] resonances.

As a final comment we would like to add that, while for the description of the inhomogeneous (quasi-static) broadening of the NMR line widths a mean-field approach has been used, it is not clear whether mean-field theory can be expected to describe the *dynamical* behaviour of $(KI)_{1-x}(NH_4I)_x$. This is because recent dielectric investigations on this mixed-crystalline system have provided evidence for an algebraic decay of the dielectric polarization [9]. In order to describe this behaviour a scaling approach was used which incorporates dynamical fluctuations that are usually neglected in mean-field treatments.

5. Conclusion

Using quadrupole-perturbed ^{127}I-NMR spectroscopy we have studied the orientational glass $(KI)_{0.56}(NH_4I)_{0.44}$. From the angular dependence of the central position as measured at room temperature significant deviations from the local cubic symmetry have been inferred. This conclusion is consistent with a C_{3v} orientation of the ammonium ion. Employing

two-dimensional separation of interaction spectroscopy it could be demonstrated that the absorption lines are only weakly broadened due to dipolar interactions ($\Delta\nu < 2.7$ kHz) but that they exhibit a pronounced inhomogeneous width. The latter is strongly temperature dependent, which is due to the combined effects of chemical shift broadening, thermal expansion of the centre of mass lattice, and, above all, local polarization freezing. The latter phenomenon is driven by the interaction of the random bonds that depend on the relative orientations of the ammonium groups. In comparison with previous NMR studies of the orientational glass $(KI)_{0.56}(NH_4I)_{0.44}$ it becomes clear that the iodine probe is particularly sensitive also to local strains. Hence the random field smearing of the freezing process, albeit weakly pronounced, becomes accessible via ^{127}I NMR.

Acknowledgment

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[17] Note that e.g. for the analysis of non-exponential deuteron relaxation the logarithm of the variance σ of a Gaussian distribution of molecular correlation times rather than σ itself scales with the stretching parameter of a Kohlrausch (cf [10]).