A Microscopic Study of Motions in Supercooled 1,3-Butanediol

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Quasielastic Rayleigh scattering of 14.4 keV Mössbauer γ-radiation has been measured on 1,3-butanediol, yielding the width Γ of the central line (assumed to be Lorentzian) and its relative intensity, for momentum transfers corresponding to molecular dimensions ($k = 0.9 \ldots 2.5$ Å^{-1}) at 243 K. $\Gamma(k)$ rises fast and then saturates. An effective correlation time τ and jump width is derived characterizing the diffusional motion of individual molecules considered as entities. Fast motions (vibrations, librations) are taken into account explicitly. The correlation time τ compares well with results from other experiments. The temperature dependence was followed from 208 up to 263 K.

1. Introduction

Rather different experimental techniques are being used to study internal motions in supercooling liquids, scattering of laser light being one of the preferred techniques today (see e.g. [1], [2]). Due to the probing fields used, and to different model assumptions, the characteristic quantities derived from the experiments are different in principle. It is our purpose here to check the results of a measurement which, by the wavelength employed, samples only regions of the order of atomic distances, against the results obtained by various other techniques, for a well studied liquid.

1,3-butanediol $CH_2OH-CH_2-CHOH-CH_3$ undercools easily down to 173 K. In the supercooled region, it has been studied by ultrasonic technique [3], by optical digital correlation spectroscopy [1], and by NMR [4]. Earlier studies of our group on glycerol [5], have used quasielastic Rayleigh scattering of Mössbauer radiation: these studies were now extended to 1,3-butanediol.

The technique employed here has its particular value because it is a scattering technique, it is sensitive to motions of the molecular backbone (C-, O-atoms), and it works on the Ångstrom scale. Furthermore, although it is restricted to broadenings which differ at most by an order of magnitude from the value set by the Mössbauer line width, its result for the characteristic time of diffusional motion bridges a gap between NMR and the other techniques mentioned.

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The present work is not concerned with what might be called the structural and bonding reasons behind, and detailed models of the types of local motion. A thorough discussion of these problems has been given for 1,5- and 2,4-pentanediol in [2].

2. Experiment

On a horizontal goniometer, well collimated 14.4 keV Mössbauer γ-radiation from a 250 mCi source (Radiochemical Centre, Amersham) $^{57}CoRh$ is scattered off the liquid, which is held between two 0.5 mm Be plates, 5 mm spacing, soldered onto a cooled brass frame [5], and surrounded by a double walled dry air chamber. Thermal gradient upwards was about 0.5 °C/cm at −70 °C, and 0.15 °C/cm at −30 °C. Commercial (Fluka AG) 1,3-butanediol (three times distilled) was used. It had a refractive index of $n = 1.4395$ at 20 °C, which compared with the literature value of 1.4418 [6], suggests water content to be $\lesssim 1.5\%$. The cell was filled and the chamber assembled in a dry glove box.

The scattered radiation is energy analyzed by nuclear resonant absorption in an enriched stainless-steel absorber (1 mg/cm^2 ^{57}Fe, FWHM = 0.6 mm/s) or – for larger quasielastic widths – by a $(NH_4)_3FeF_6$ absorber (8 mg/cm^2 ^{57}Fe, FWHM = 1.5 mm/s). Figure 1 presents some examples. Measuring times were between one and twenty days. The combined source-detector, i.e. apparatus, profile was measured by (200)-Bragg scattering from a LiF crystal ($f' = 0.993$).

The line shapes fitted to the experimental results were a convolution of a sum of Lorentzians (for the

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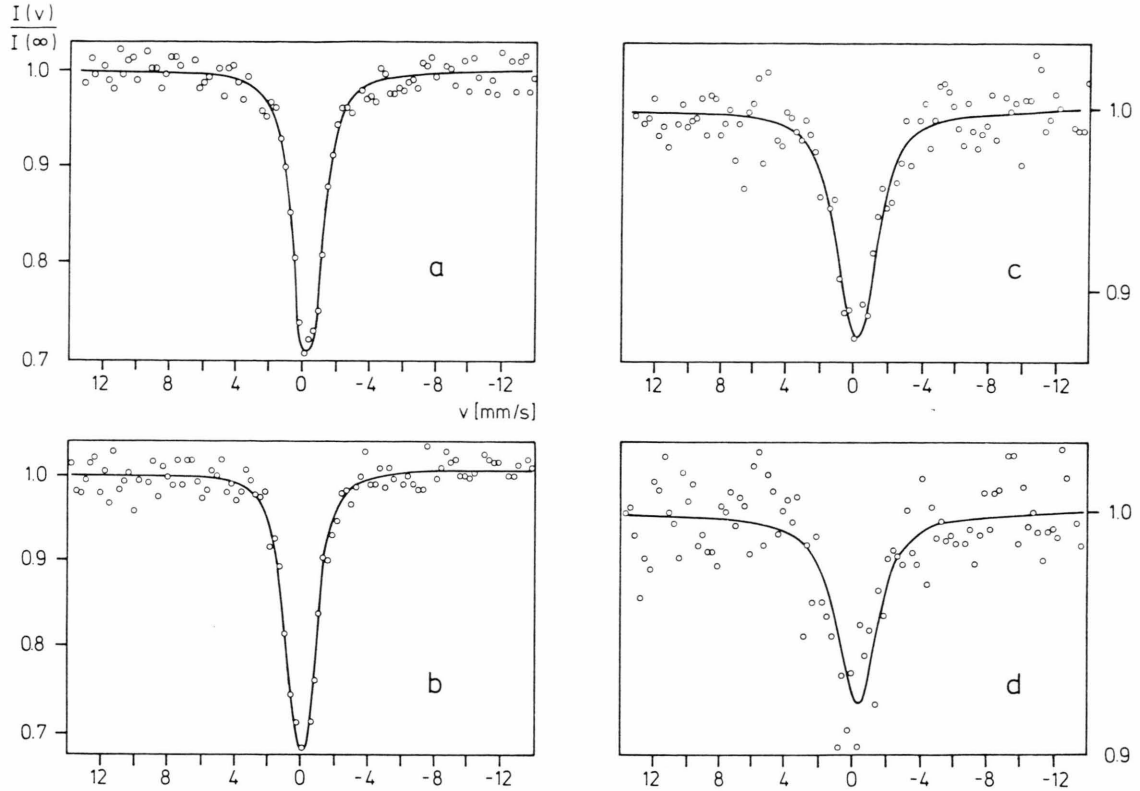

Fig. 1. Mössbauer spectra of 1,3-butanediol for scattering angles of 4.75° (a), 5.5° (b), 7.5° (c), and 10.0° (d) at −30 °C.

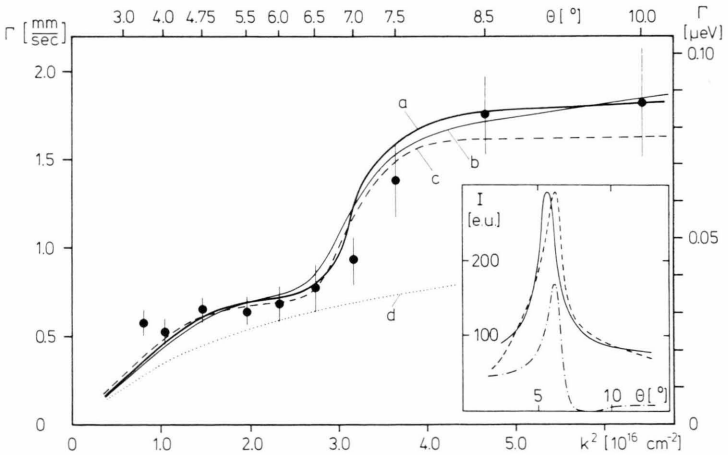

Fig. 2. Quasielastic linewidth Γ for 1,3-butanediol at −30 °C. Each Γ is a mean value from two to five spectra. For curves a–c, refer to Figure 3. Curve d is the translational width, see text. Inset: $I_{tot}(q)$ from Debye-Scherrer-experiment (full line) and from the model structure (dashed). The distinct term (the $A_0(k) \cdot F_d(k)$ contribution) is shown as dash-dot line.

apparatus profile) with a single Lorentzian for the quasielastic scattering, the latter characterized by full width at half maximum FWHM = $\Gamma(k)$ and area $I_q(k)$; $k = 4\pi\lambda^{-1}\sin\theta/2$. To determine the quasielastic fraction $f'(k) = I_q(k)/I_{tot}(k)$, the total intensity $I_{tot}(k) = I_{in}(k) + I_q(k)$ was measured by raising the maximum velocity to > 20 cm/s.

Since the curve $I_{tot}(k)$ is k-broadened due to the angular width of the Mössbauer setup [5], it was also obtained on a conventional Debye-Scherrer

apparatus using Mo K_α radiation, see inset of Figure 2. – The finite angular resolution shifts the $\Theta = 3°$ point for $I_q(k)$ and $\Gamma(k)$ by $+0.5°$, as derived from calculated test spectra. – The Compton correction was taken from [5].

3. Analysis of Results

3.1. Model

The supercooled molecular liquid is described as in [5] by rigid molecules of one configuration, the spatial center of mass correlation being taken from a hard sphere Percus-Yevick radial distribution function [7]. Translational as well as rotational diffusion are treated as isotropic, independent random walk processes with finite mean square step sizes, $\langle r^2 \rangle$ and $\langle \varepsilon^2 \rangle$, respectively, and with identical correlation time τ. The resulting translational and rotational diffusion constants are $D = \langle r^2 \rangle / 6\tau$ and $\mathscr{D} = \langle \varepsilon^2 \rangle / 6\tau$, respectively. The quasielastic intensity $I_q(k)$ consists then of a translational term (static formfactor $F_d(k)$) and a rotational term, the latter being a sum over l-components ($l = 1, 2, \ldots$). These derive from a multipole expansion of the electron density of the molecue (coefficients $A_l(k)$), and contribute Lorentzians which have increasing line widths and decreasing intensities for increasing l:

$$I_q(k, \omega) \sim A_0 [F_d(k) + 1] \frac{W/2\pi}{\omega^2 + (W/2)^2} + \sum_{l=1}^{\infty} A_l(k) \times \frac{W_l/2\pi}{\omega^2 + (W_l/2)^2}, \quad (1)$$

$$W = \frac{2k^2 D}{1 + k^2 D\tau}, \quad W_l = W + \frac{2l(l+1)\mathscr{D}}{1 + l(l+1)\mathscr{D}\tau}. \quad (2)$$

The molecular formfactors needed ($F_d(k)$ and $A_l(k)$) were calculated for various assumed configurations of 1,3-butanediol which were derived from the known structure of n-butane [8]. By a trial and error procedure, fair agreement was obtained for one configuration, between

$$\left[A_0(k)\, F_d(k) + \sum_0^{\infty} A_l(k) \right]$$

and the measured $I_{tot}(k)$, see inset of Fig. 2 and Table 1. The terms $F_d(k)$ and $A_l(k)$ turn out to be similar to those for glycerol [5]. Of course, these simple model calculations imply no more than that the static structure factor corresponds reasonably well to one configuration *on the average*.

Table 1. Parameters used to describe the structure factor $I_{tot}(k)$ of liquid 1,3-butanediol at 25 °C.

PY hard sphere liquid:	packing fraction	$\eta = 0.49$
	sphere diameter	$d = 4.25$ Å

Molecular configuration of
$C^{(1)}H_2O^{(1)}HC^{(2)}H_2C^{(3)}HO^{(2)}HC^{(4)}H_3$, (xyz) positions in Å

$O^{(1)}$ (0.8 0.7 2.0)	$C^{(1)}$ (1.6 1.4 1.0)	$C^{(3)}$ (3.7 0.4 0.0)
$O^{(2)}$ (3.9 0.2 1.4)	$C^{(2)}$ (2.2 0.4 0.0)	$C^{(4)}$ (4.3 1.8 0.0)

Fast motions (intramolecular or of entire molecules) i.e. large energy transfers, are included globally as inelastic scattering $I_{in}(k)$. – For details, the reader is referred to [5].

From our model calculations, from the value of the molecular size d obtained in the fit of the Percus-Yevick solution to the present data, and from the results of a more detailed study [9] it appears reasonable to conclude that scattering from the centre of mass correlations ($F_d(k) \cdot A_0(k)$ term) does indeed peak at the observed structure maximum, and that it contributes at least 50% to the total scattering in this k-region (the remainder is virtually all $l = 2$). This makes the use of one single Lorentzian for the broadening a rather good approximation. Beyond $k \approx 2 \cdot 10^8$/cm essentially all scattering appears to be caused by A_l with $l \geqq 1$, i.e. by deviations from sphericity, the orientations of which we assume to be uncorrelated between molecules.

3.2. Quasielastic scattering as a function of momentum transfer

Velocity spectra were measured for $k^2 = 0.8\,\text{Å}^{-2} \ldots 6\,\text{Å}^{-2}$ at one fixed temperature, $T = 243$ K. In the region $k^2 < 2.3\,\text{Å}^{-2}$, both absorbers were used and identical results obtained. The results $\Gamma(k)$ are presented in Figure 2.

The parameters wanted, $\langle r^2 \rangle$, τ, and $\langle \varepsilon^2 \rangle$, were obtained as follows: Quasielectric spectra $I_q(k, \omega)$ were calculated from the analytic expression (1) and (2) assuming one set of the parameters. The FWHM was read off each spectrum and a curve $\Gamma(k)$ produced. These curves were then compared by eye with the experimental data $\Gamma(k)$ and accepted or rejected. Three accepted curves are included in Figure 2. Agreement is good in general, but the

point at 3.5° appears to be definitely too high; no reason for this discrepancy is known. The dotted curve in Fig. 2 represents the translational contribution to the total broadening: it is calculated using the "best" parameters $\tau = 21 \cdot 10^{-9}$ s and $\langle r^2 \rangle = 2.2$ Å^2, but $\langle \varepsilon^2 \rangle = 0$.

The correlation between the parameters leads to an allowed region in $\langle \varepsilon^2 \rangle$, $\langle r^2 \rangle$, τ-space which is sketched in Figure 3. The best fit is at $\tau = 21 \cdot 10^{-9}$ s; the possible ranges of parameters yield for 1,3-butanediol at $T = 243$ K

$$\tau = (21 \pm 6) \cdot 10^{-9}\,\mathrm{s}\,. \tag{3}$$

This effective correlation time is included in Fig. 6 and will be discussed in Section 4.

Furthermore, $D = (1.7 \pm 0.4) \cdot 10^{-9}$ cm^2/s is obtained. The rotational diffusion constant $\mathscr{D}$ is very uncertain, mostly because large values of $\langle \varepsilon^2 \rangle$ give a formally acceptable fit even though they are unreasonable (see Figure 3). $\mathscr{D} > 0.5 \cdot 10^7$ rad^2/s can be stated safely, and most probably $\mathscr{D} \approx 2 \cdot 10^7$ rad^2/s.

The Debye-Waller-factor $f'(k)$ is presented in Figure 4. To demonstrate its sensitivity to model assumptions, we have included two calculated curves assuming a purely translational or purely rotational cause for $f'(k)$; we conclude that

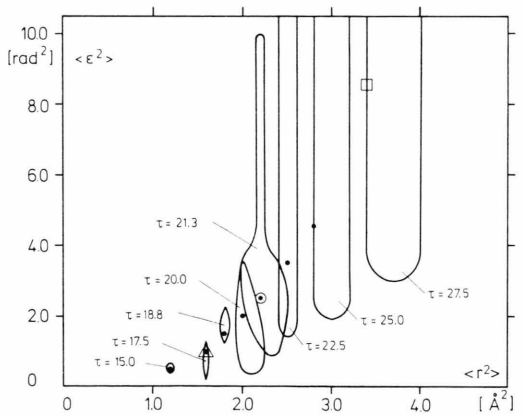

Fig. 3. The range of possible fit parameters τ, $\langle \varepsilon^2 \rangle$, $\langle r^2 \rangle$ for $\Gamma(k)$ in Fig. 2 is demonstrated by projecting onto the $\langle r^2 \rangle$, $\langle \varepsilon^2 \rangle$ plane eight cuts $\tau = \text{const}$, τ in 10^{-9} s. For each value of τ, the dot is at the best agreement. The parameter set marked ○ gives curve a) of Fig. 2, best agreement of all sets of parameters, △ curve b), and □ curve c). τ values beyond about $15 \cdot 10^{-9}$ s and $28 \cdot 10^{-9}$ s yield a clear discrepancy with experimental curve $\Gamma(k)$. Note that the series of dots and △, ○, □ delineate an essentially one dimensional range of "best" combinations of fit values for τ, $\langle r^2 \rangle$, $\langle \varepsilon^2 \rangle$.

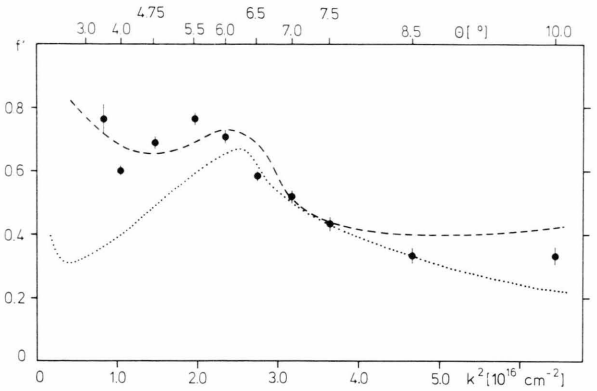

Fig. 4. Fraction $f'(k)$ of total scattering which is quasielastic, for 243 K. Dotted model curve: Only fast motion of the center of mass $f'_{\mathrm{trans}} = \exp(-k^2\langle x^2 \rangle$ with $\langle x^2 \rangle = 0.23$ Å^2. Dashed curve: Reduction of $l = 2$ term by fast libration, $f'_{\mathrm{lib}} = \exp(-l(l+1)\langle \Phi^2 \rangle)$ from [5], with $\langle \Phi^2 \rangle^{1/2} = 22°$.

$\langle x^2 \rangle^{1/2} < 0.5$ Å and $\langle \varepsilon^2 \rangle^{1/2} < 0.4$ rad are upper limits for the amplitudes of the fast c.m. vibration or fast libration, respectively.

3.3. Temperature dependence at the structure maximum

At the maximum of the $I_{\mathrm{tot}}(k)$-curve, $\Theta = 5.5°$ or $k = 1.40$ Å^{-1}, we have measured the temperature dependence of the broadening (Γ) and the quasielastic fraction (f') from 263 K to 208 K.

The quasielastic broadening Γ obtained at the $I(k)$-maximum, which is mainly determined by translationl diffusion, probably receives most of its temperature dependence from the temperature dependence of the correlation time τ, as e.g. also in glycerol [5], rather than from $\langle r^2 \rangle$. We can therefore estimate the temperature dependent "effective correlation time" by using throughout the value determined at 243 K, $\langle r^2 \rangle = 2.2$ Å^2. The result appears in Fig. 6 as small dots.

The quasielastic fraction f' was used to derive an effective mean square amplitude $\langle x^2 \rangle$ from $f'(k) = \exp[-k^2\langle x^2 \rangle]$, see Figure 5. We have added a rough estimate for the thermal displacements of the molecular center of mass due to acoustic modes

$$\langle x^2 \rangle = \frac{3 k_{\mathrm{B}} T}{m v_{\mathrm{s}}^2 k_{\mathrm{D}}^2}\,, \tag{4}$$

where m is the molecular mass ($1.496 \cdot 10^{-25}$ kg), v_{s} the sound velocity taken from [3], and $k_{\mathrm{D}} = \pi/d$.

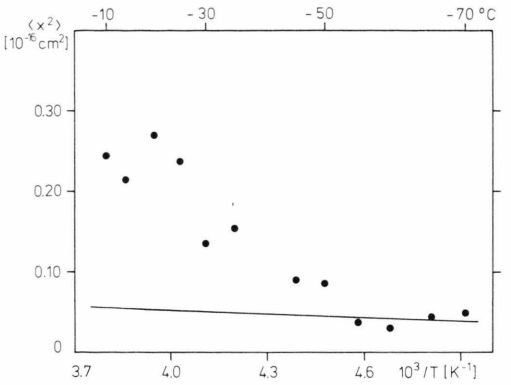

Fig. 5. Effective fast motion amplitude $\langle x^2 \rangle$ at $k = 1.4$ Å^{-1}. The full line is the lower estimate from (4).

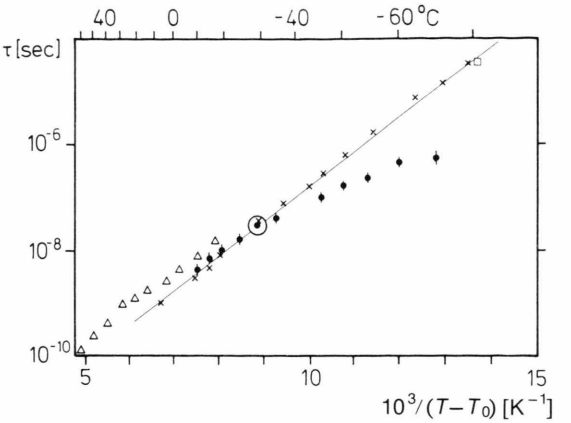

Fig. 6. Effective correlation times for 1,3-butanediol as derived in different experiments: ○ present work, correlation time and jump width at 243 K derived from the data of Figure 2. ● present work; correlation time derived under the assumption that the jump widths are the same as at 243 K; △ NMR relaxation [4]; × Ultrasonics data [3] as presented in [1]; □ Optical digital correlation spectroscopy [1]. The latter data [1] extend down to -100 °C, $\tau = 10^2$ s, and the line is drawn to follow those points. – The Vogl-Fulcher temperature is taken as $T_0 = 130$ K from [1].

The following results are pointed out here: a) fast motions increase with T, but this increase is much slower than that of the diffusional width Γ. b) The fast amplitude $\langle x^2 \rangle^{1/2}$ derived is about a factor of three smaller than the step size $\langle r^2 \rangle^{1/2}$. c) The relation between fast and diffusional motion is similar to that in glycerol [5], another supercooling aliphatic alcohol: The value $D = 2 \cdot 10^{-9}$ cm^2/s is connected with the same fast displacement $\langle x^2 \rangle = 0.15$ Å^2, however there are larger slower steps in butanediol ($\langle r^2 \rangle = 2$ Å^2, $\tau = 0.2 \cdot 10^{-7}$ s) than in the smaller molecule glycerol ($\langle r^2 \rangle = 0.8$ Å^2, $\tau = 0.07 \cdot 10^{-7}$ s).

4. Discussion: Comparison with other Experiments

A comparison of the dynamics of molecular motion in supercooled 1,3-butanediol as revealed in NMR [4], in optical correlation spectroscopy [1], in ultrasonics [3] and in quasielastic scattering of Å-waves (present work) appears possible only by comparing the "effective" correlation times. The NMR work and the present work base their interpretation essentially on a random walk diffusional model, they are sensitive to travel distances in the Ångstrom region. Optical intensity correlation work and ultrasonic work both based their analysis on the model of a viscoelastic medium; a distribution of relaxation times was introduced as usual in these experiments, and the description included no further model assumptions.

We compare the results for τ in Fig. 6, using a Vogl-Fulcher plot where T_0, the temperature of disappearing transport, is 130 K [1]. The data are seen to fall rather closely on the single line which connects optical with NMR data over about twelve decades of τ.

At $T \lesssim 220$ K, a systematic deviation of the present results from the general trend develops. We consider this as rather probably due to a combination of deficiencies of our method of measurement and analysis: The broadening falls below 10% of the line width; also the separation of quasielastic and inelastic scattering becomes less clear. Furthermore, the q-dependence of Γ was not measured, and we have neglected any temperature dependence of $\langle r^2 \rangle$.

From a quasielastic neutron scattering experiment on glycerol using the same model and method of analysis it is known that results for Γ become systematially distorted (increased) if the broadening Γ falls below roughly 10% of the total apparatus linewidth [10]. This happens here at $T \lesssim 220$ K. We conclude that we have to consider those results as less reliable, and shall omit them from the discussion.

The presence of fast motions for which different experiments apply corrections in different ways, appearently does not disturb our derivation of the slow correlation time τ. In fact an advantage of the Mössbauer scattering technique shows up in the treatment of fast motions because they are mea-

sured directly as inelastic intensity (yielding a total formfactor). This is superior to the other methods and may be essentially valuable for slow diffusing or amorphous systems, where the time scales for slow and fast motions are separated even more than for the present case.

In NMR these fast motions show up in the fact that the frequency integral of the relaxation rate $1/T_1(\omega)$ becomes markedly temperature dependent (see e.g. [11] and for a discussion [12]); in the ultrasonic studies, uncertainties as to the high frequency behaviour caused by the limited dynamical range are reflected e.g. in the discussion of "hysteresis" and M_∞ in [1] and [3].

In conclusion it can be stated that an almost perfect agreement exists between the slopes of the four methods compared in Figure 6. Possibly more relevant, there is also essentially perfect agreement between three methods and the extrapolation of the fourth in absolute values. Our most thoroughly studied point ($T = 243$ K) is situated in that junction area. It appears thus established that the methods NMR, optical digital correlation spectroscopy, ultrasonic relaxation, and Mössbauer scattering yield identical results for the effective slow correlation time of a supercooled glassforming liquid, even such a complicated one as butanediol. To this list of experiments may be added quasielastic incoherent neutron scattering, since its results were found to agree with Mössbauer scattering for the case of supercooled glycerol, see [10], at the highest resolutions.

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