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L. Q. Amaral and L. A. Vinhas

CENTRO DE OPERAÇÃO E UTILIZAÇÃO DO REATOR DE PESQUISAS
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MOLECULAR DYNAMICS OF *TERT* BUTANOL STUDIED BY NEUTRON INELASTIC SCATTERING[1]

L Q Amaral[2] and L A Vinhas[3]

ABSTRACT

Molecular dynamics of *tert* butanol in two crystalline phases and in the liquid state was investigated by cold neutron scattering in the temperature interval 8-35°C Inelastic spectra remained essentially the same indicating short range order in the liquid state A frequency spectrum obtained from the sum of seven Gaussian functions fitted the measured time-of flight distribution and allowed assignment of peak positions A barrier $V_1 = 4.0 \pm 0.2$ kcal/mol for CH_3 internal rotation was obtained results are compatible with a second order term $V_2 = -0.1 V_1$ Quasielastic line broadening and Debye-Waller factors were analysed in terms of models for molecular diffusion and the results compared with NMR data It is concluded that cooperative rotational diffusion occurs both in solid and liquid states.

I – INTRODUCTION

Molecular compounds that form structures with different phases are receiving increasing attention specially if the phase transition involves a change in rotational dynamics [1 2] as occurs with the so called organic globular compounds[3] The molecules involved are almost spherical in shape and show in the solid state a phase transition with large entropy change from a crystal II form of low symmetry stable at low temperature to a crystal I form with high symmetry and a certain degree of plasticity the entropy of melting is very small usually less than 5 e u following Timmermans's convention and the triple point is high The peculiar physical properties of the "plastic" crystal phase have been attributed to orientational disorder and rotation of the molecules about their lattice positions[3 5] Although what actually happens is a small resistance to molecular reorientations and very seldom free rotation the solid transition and the plastic phase are sometimes called rotational

Compounds of the type $(CH_3)_3CX$ that show also internal methyl rotation, fall usually among the plastic crystals and have been studied[3] for X = Cl Br I CN SH *tert* Butanol $(CH_3)_3COH$ has been classified[6] as a globular compound due to its small entropy of fusion This compound has a high melting point for the alcohol series (25°C) and a first order phase transition at 13°C, studied by calorimetry[7] and dilatometry[8] Heat capacity measurements indicate the existence of a crystal III form over the temperature range 8 5-21 5°C as an alternative option that could not be reproduced at will Dilatometric studies mention an oldness effect of crystal I Entropy results[7] show that the phase transitions are not highly energetic which makes questionable the 'plastic' character of the compound that besides has complex crystalline forms. The internal rotation of the methyl groups has been studied by thermodynamic measurements in the gas state[9], by NMR in the liquid state[10], by far infrared in the solid state[11], and by neutron transmission in the condensed state[12]

The neutron transmission studies performed at this laboratory[12], confirm the existence of a crystal III phase but this is difficult to reproduce furthermore this work shows that the most important

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2 Instituto de Física Universidade de São Paulo C.P 20516 São Paulo Brasil
3 Instituto de Energia Atômica São Paulo Brasil
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dynamical change occurs at the change of state and not at the phase transition The small entropy of fusion may be due more to ordering in the liquid than freedom in crystall I and could be related to the presence of H bonding NMR measurements indicate[13] the existence of cyclic trimers in the liquid and there is evidence of association even in the gas state[9]

In order to investigate further the molecular dynamics of *tert* butanol in the low frequency region neutron inelastic scattering experiments were performed in the temperature interval 8 35°C

II – EXPERIMENTAL

Measurements were taken with a conventional cold neutron time-of flight spectrometer[14] at the IEA 2 MW swimming pool research reactor A polycrystalline beryllium filter cooled with liquid nitrogen transmits a neutron spectrum with a sharp cutoff at 3 95 Å (5 2 meV) and with mean energy of 3 5 meV and width 2 meV a Pb monocrystal filter is used to reduce γ ray background Neutrons scattered by the sample at angle Ω are pulsed by a curved slit slow neutron chopper operated usually at 13 000 rpm and are detected by a bank of ^{3}He detectors after an evacuated flight path of 3 15 m. Scattered neutron spectra are recorded with a multichannel time-of flight analyzer and the time-of flight resolution is 1 7% for 4 Å neutrons and 6 4% for 1 Å neutrons

The sample was commercial Merck *tert* butanol of 99% purity and 0 1% maximum water content The scattering sample sealed in an aluminium holder while in the liquid state has a tickness of 0 2 mm ensuring a 90% transmission to avoid multiple scattering and it is placed at 45° to the incident beam The sample temperature was controlled within 2°C

Energy gain spectra were collected at scattering angles Ω between 20° and 90° Spectra in the liquid state were measured at 30°C in five scattering angles In the solid state six spectra were obtained at 15°C in three scattering angles and six independent spectra were obtained at 9°C in one scattering angle varying the thermal treatment of the sample This was made because transmission measurements[12] showed the influence of the thermal treatment in obtaining a possible crystal III Some series refer to simple cooling while in others the sample stayed several hours at liquid nitrogen or dry ice before starting the measurements Owing to the reactor schedule (40 h/week) each spectrum takes two or three weeks to be obtained monitoring of the incident beam was used over such long periods to estimate relative intensities

After subtraction of background and sample holder scattering spectra were corrected for chopper transmission air scattering and detector efficiency, all these corrections are energy dependent A typical result for the time-of flight distribution $d^2\sigma/d\Omega dt$ for crystal I at $\Omega = 50°$ and $T = 15°C$ is shown in Figure 1

III – RESULTS AND DISCUSSION

Inelastic spectra remain essentially equal on the three phases there is a sensible variation only for small energy transfers and in the width of the quasielastic peak

For the analysis of scattered spectra a separation between quasielastic and inelastic scattering must be performed Usually this separation is made by simple extrapolation of the inelastic contribution another method is to estimate the inelastic contribution by a Krieger Nelkin model As the errors in both methods are essentially the same[15] a simple extrapolation was adopted, with evaluation of a maximum and minimum inelastic slope under the quasielastic peak

A – Determination of Frequency Spectra

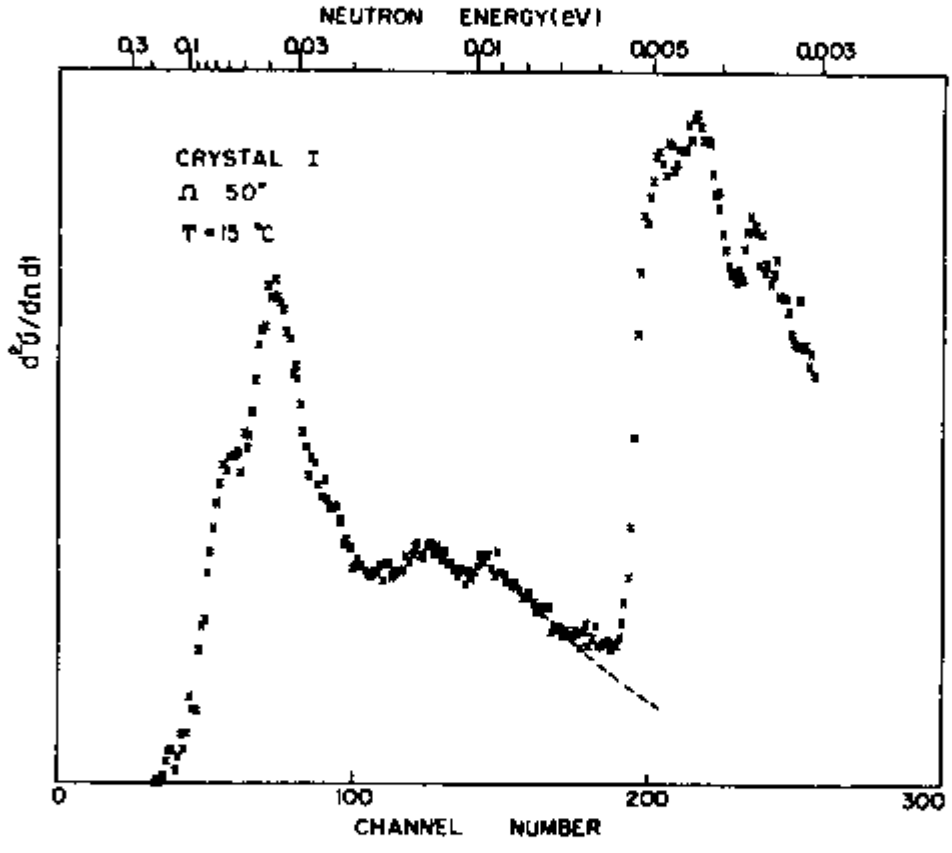

Figure 1 — Typical Result of Corrected Time-of Flight Spectrum $d^2\sigma/d\Omega dt$ (counts) as a Function of Channel Number With Corresponding Neutron Energy Dashed Line Shows Adopted Separation Between Inelastic and Quasielastic Scattering

For the analysis of the inelastic scattering, a reduction to generalized frequency spectra plots was performed in order to eliminate distortions present in the $d^2\sigma/d\Omega dt$ experimental spectrum. This allows a most precise determination of the peak positions.

The scattering by hydrogeneous compounds corresponds essentially to incoherent scattering by H atoms since the incoherent scattering cross section of the H atom is about 20 times that for C and O.

Defining the energy transfer $\hbar\omega = E - E_0$ and the wave vector transfer $Q = k - k_0$ a generalized frequency spectrum for solids can be obtained from the measured time-of flight distribution from[16 18]

$$Z(\beta) \sim e^{2W} \frac{\hbar\omega}{(\hbar Q)^2} \left[1 - \exp\left(\frac{\hbar\omega}{kT}\right)\right] E^{-1} \frac{d^2\sigma(\Omega\, t)}{d\Omega dt}$$

where e^{2W} is a generalized Debye-Waller factor and $\beta = \hbar\omega/kT$. $Z(\beta)$ for molecular crystals must be interpreted as an effective frequency spectrum that corresponds to the density of states modulated by the square of the vibrational amplitudes. Thus translational and rotational components enter with different weights and neutron scattering results are mostly sensible to torsional motions of small groups containing H atoms.

This same formalism can be extended to the liquid state if e^{2W} is interpreted as a generalized factor substituting the usual limit for $Q \to 0$. In this case W may vary with energy. Since the factor e^{2W} is unknown, the experimental results give after straightforward transformation a function $G(\beta) \sim Z(\beta)\, e^{-2W}$.

Figure 2 shows some typical $G(\beta)$ spectra. Calculations have been performed assuming for E_0 the mean energy of the cold incident spectrum.

A careful analysis of $G(\beta)$ curves for all scattering angles and for the three phases revealed that the position of peaks and valleys remained constant within 2%; these positions are shown in Table I. The relative intensities varied, but the analysis will concentrate on the peak positions.

Table I

Analysis of Generalized Frequency Spectra Obtained from Neutron Inelastic Scattering. Position in the Measured $G(\beta)$ Remain Equal for the Different Phases Within 2%

		Deconvoluted $G(\beta)$		
	Measured $G(\beta)$ (meV)	Gaussian peak (meV)	Gaussian width (meV)	Resolution (meV)
		2 6	2 4	0 05
Peak	6 0 ± 0 1	4 5	1 7	0 14
Peak	9 3 ± 0 2	7 4	3 0	0 29
Valley	14 ± 0 5	11 6	7 3	0 57
Hump	20 ± 0 5	18 7	4 2	1 18
Peak	33 ± 1	31 1	19 4	2 50
Peak	58 ± 1	57 8	29 1	6 33

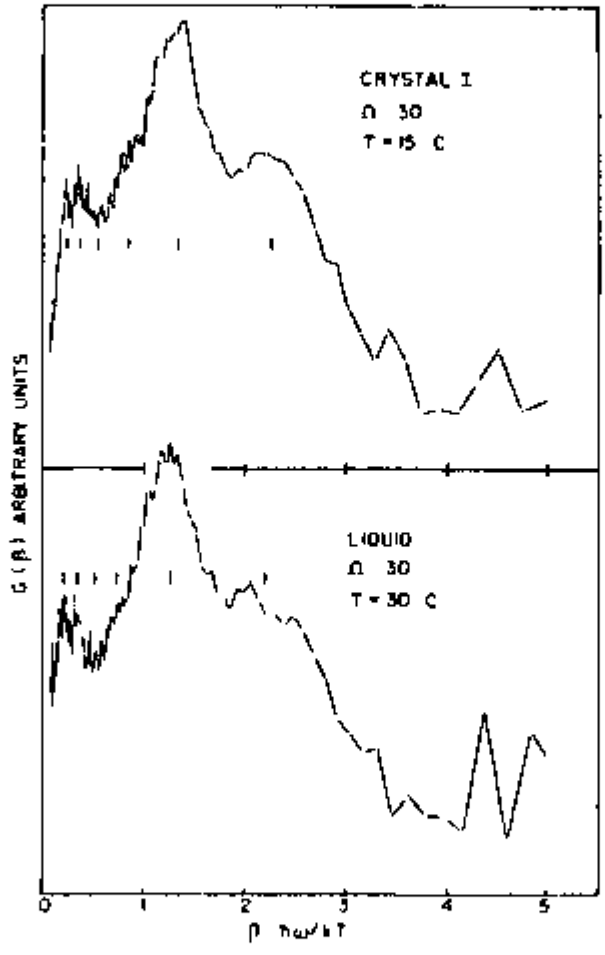

Figure 2 – Typical Results for Generalized Frequency Spectra $G(\beta)$ in Function of $\beta = \hbar\omega/kT$ Positions of Peaks and Valleys Remain Equal Within 2%

To analyze the effect of the real incident spectrum one of the experimental results in the solid state has been fitted to a theoretical curve obtained assuming $G(\beta)$ to be a sum of Gaussian functions A computer program has been developed to calculate $d^2\sigma/d\Omega dt$ from a chosen set of Gaussian functions and perform the convolution with the E_0E incident spectrum The expression of $G(\beta)$ as a sum of Gaussians is a mathematical artifice to obtain an analytical form for $G(\beta)$ but it can have a physical meaning in the case of well separated energy levels An iterative process was performed until a good adjustment was obtained with $G(\beta)$ expressed as a sum of seven Gaussian functions seen in Figure 3 The sensibility of the parameters adjustment is 2%

Table I shows also the best Gaussian parameters (peak position and width at half height) after deconvolution Results show that if one neglects the real shape of the incident spectrum a distortion of ~ 1 meV is obtained For a peak observed at 5 meV this means an error of 20% in the peak position The sum of Gaussians has not been corrected for the spectrometer resolution whose values are also shown in Table I The comparison of the resolution with the Gaussian widths shows that all peaks present intrinsic broadening thus none can be considered as a simple transition between well defined energy levels

The peak at 33 meV very well pronounced and dominant in the neutron spectrum must be associated to the $1 \rightarrow 0$ transition of CH_3 torsional motions to which the $2 \rightarrow 1$ transition is superposed The peak at 58 meV corresponds to the $2 \rightarrow 0$ transition superposed to skeletal molecular movements Far infrared low temperature data[11] are consistent with this assignment Characteristic vibrations of the $(CH_3)_3C$ structure as well as C C-O and C C C bend occur[9 11 19] around 50 meV but they are not expected to contribute significantly to neutron scattering In the region of 80 meV where a OH torsion is expected the intensity is already too low due to the population factor The butanol molecules are attached through hydrogen bonds at the OH groups and the 20 meV peak corresponds to the stretching frequency of these hydrogen bonds as observed by ir[20 11] The valley at 14 meV probably separates the regions of internal and external modes The peaks at 6 and 9 meV may be of translatory or librational origin

The fact that positions of the peaks remain constant in the three phases indicates that no drastic alteration in the interaction potentials occur This means that short range order must be kept in the associated liquid similar indications were obtained in the analysis of Raman intensities[21]

In two series extra peaks were observed shown in Figure 4 These two spectra were obtained in the solid state in measurements where it has been difficult to keep the sample temperature, due to electric power failures There is not enough basis to associate these different results with the possible cystal III form These extra peaks correspond to two of the Gaussians of $G(\beta)$, that could have been enhanced by a preferred macroscopic orientation of crystallization[18] The possibility of existence of a third crystalline form remains open

B — Internal CH_3 Rotation

The determination of the barrier hindering methyl rotation from the observed energy transitions has been discussed by Fateley and Miller[22] The barrier has the form

$$V(\alpha) = \tfrac{1}{2} V_3 (1 + \cos 3\alpha) + O^3 (V_3)$$

In the case of one simple CH_3 group the second order term may be neglected since it represents less than 3% of the main potential[22 23] In the case of two or more CH_3 groups the second order term represents the interaction between the CH_3 groups and may be of the order of 10% or more[24]

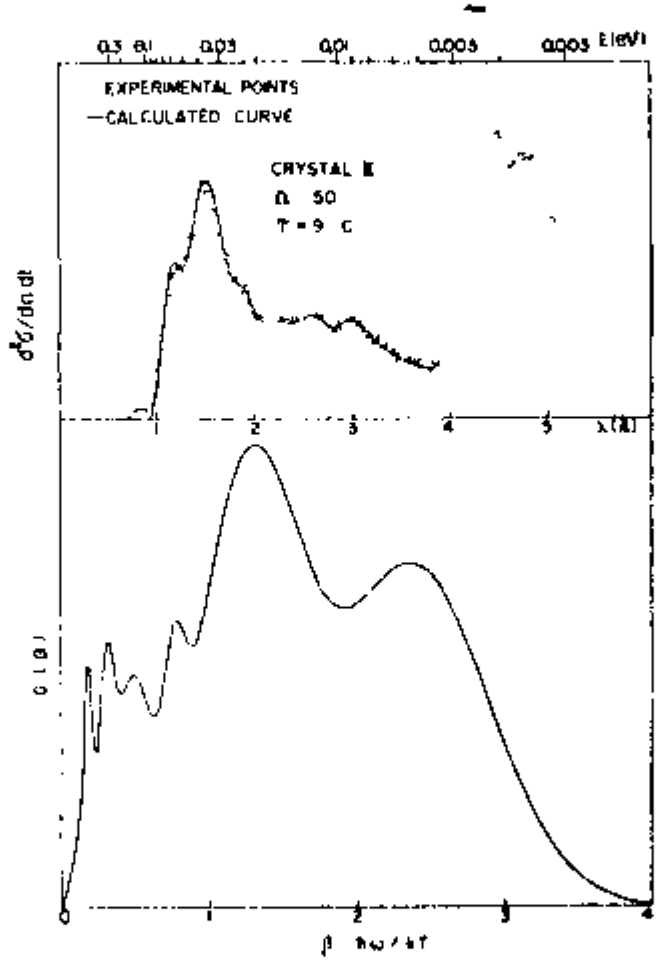

Figure 3 — Measured Spectrum $d^2\sigma/d\Omega dt$ for Crystal II and Calculated Curve as a Function of Neutron Wavelength With Corresponding Neutron Energy. The Lower Figure Shows $G(\beta)$ Function (Sum of Seven Gaussian Functions) from Which the Calculated Spectrum in the Upper Figure Was Obtained

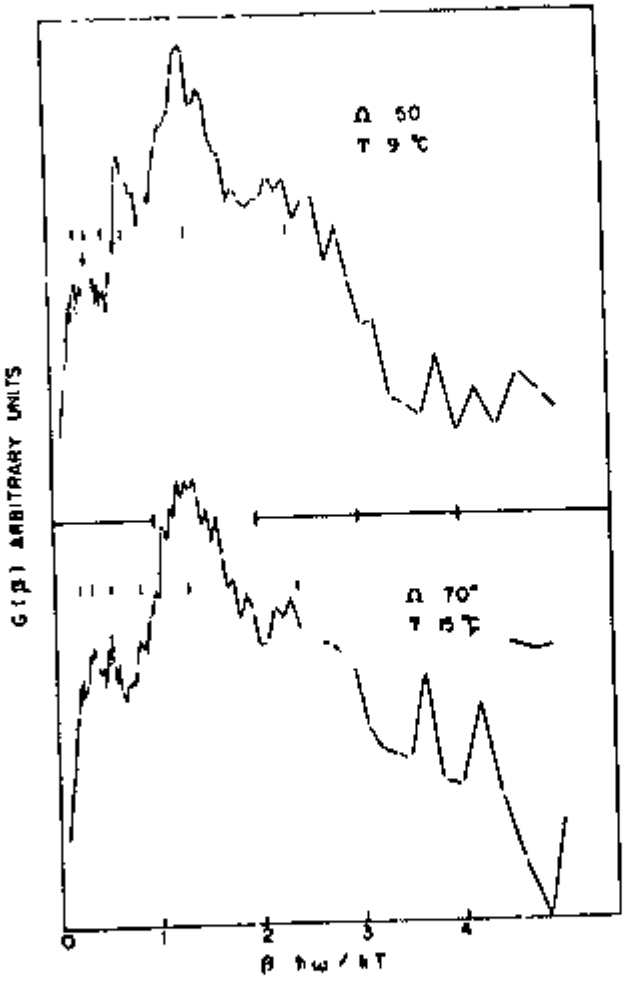

Figure 4 — Abnormal Results for $G(\beta)$ That May Indicate the Obtention of a Crystal III Phase

Taking into account only the first order term the observed transition allow the determination of V_1[22 25] utilizing for the reduced CH_3 moment of inertia the value[9] 5.145×10^{-40} g cm^2. For the $1 \rightarrow 0$ transition at 31 meV the adimensional parameter $S = 115$ gives $V_1 = 4.0 \pm 0.2$ kcal/mol. The value obtained is in good agreement with the infrared estimative[11] of 4.1 kcal/mol and is consistent with previous estimates from neutron transmission data[12] and NMR results[10].

For *tert* butanol a nonnegligible second order term $V_2 < 0$ is expected as occurs with other compounds with more than one CH_3 group[22 24]. This term would be responsible for a compression of the torsional levels and a splitting of the sublevels A and E that can be resolved only with high resolution neutron spectrometers[24]. However the consideration of the broadening of the peak may help to estimate V_2. This broadening is probably due to an actual separation between the two energy levels which is expected to be ~ 20% for methyl groups bound to a C atom[22 24] and is of 17% for the low temperature data[11]. A separation between the levels of that order together with the experimental resolution could explain the observed broadening of the peak. This would correspond to $V_2 \sim 0.1 V_1$. A coupling between the CH_3 torsional oscillations and the skeletal motions of the $(CH_3)_3C$ group could also contribute to the observed broadening.

The agreement between the value 4.0 ± 0.2 kcal/mol here obtained with the thermodynamic result for the gaseous state[9] 3.8 kcal/mol as well as the fact that the peak position does not change in the phase and state transitions evidence that this barrier is practically independent of intermolecular forces. Comparison of results for *tert* butanol with microwave results[23] for $(CH_3)_3CH$ and $(CH_3)_3CF$ respectively 3.9 and 4.3 kcal/mol indicates that the barrier is essentially determined by the interaction forces of the $(CH_3)_3C$ group. Only when the C atom is substituted for instance by P the barrier is considerably reduced.

C — Quasielastic Scattering

The inelastic scattering being practically insensible to the phase transitions any information about changes in rotational freedom can be obtained only from the analysis of the broadening of the elastic line. The study of this broadening is usually performed admitting that the cross section is a Lorentzian function of energy this assumption finds support in many theoretical considerations and dynamical models[14 17]. Only with high resolution spectrometers is it possible to study in greater detail the exact form of the cross section curve[26].

A calibration curve has been obtained[14] relating the Lorentzian half width ΔE with the observed broadening δt of the beryllium edge after a double convolution with the real incident spectrum and the spectrometer resolution. A fitting of the measured spectra with this theoretical convolution was also performed and a typical result is shown in Figure 5. Figure 6 shows the results obtained for ΔE in function of Q^2.

An estimative was made for the relaxation time for internal CH_3 rotation[14] giving a value of $\sim 10^{-10}$ s for the liquid state, NMR results[10] gave 0.4×10^{-10} s. Residence times of this order correspond to broadenings of the order of the errors in the measured ΔE for liquid and crystal I. It is therefore assumed that the CH_3 contribution can be neglected in the liquid and crystal I phases and the observed broadening is due to motions of the whole molecule that correspond to a superposition of translational with rotational diffusion as felt in the neutron time scale.

In general a linear dependence of ΔE with Q^2 is obtained in the case of simple diffusion and a constant value of ΔE indicates jump diffusion. Our results do not indicate a saturation behavior at least in the measured Q^2 range.

Information about the type of rotational motion can be obtained from the Debye-Waller factor ($2W = a^2 Q^2$) that governs the intensity of the quasielastic peak. The values experimentally determined for the liquid and crystal I are respectively $a^2 = (0.26 \pm 0.05)$ Å^2 and (0.18 ± 0.04) Å^2.

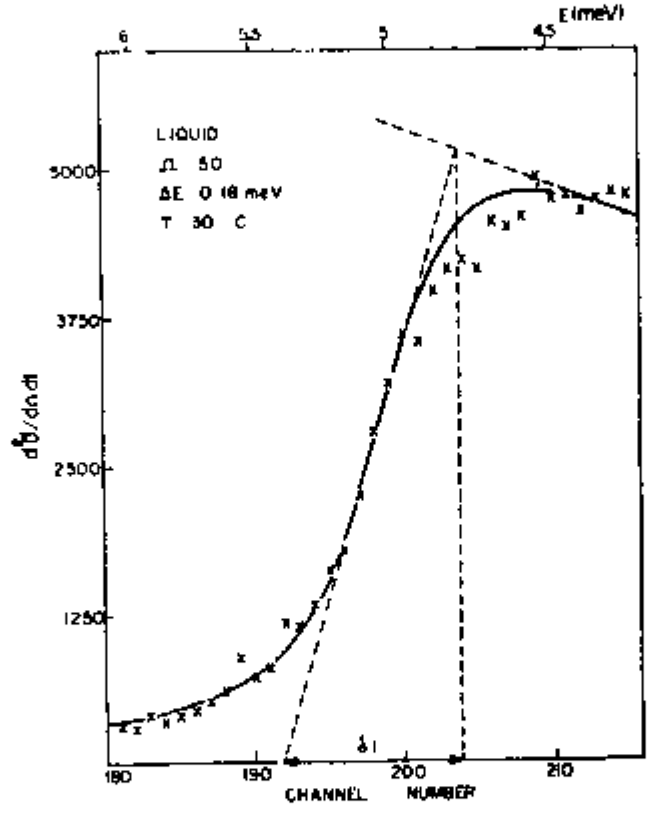

Figure 5 — Typical Result for Quasielastic Scattering $d^2\sigma/d\Omega dt$ as a Function of Channel Number With Corresponding Neutron Energy Dashed Line Illustrates Experimental Determination of the Broadening δt that Yields Same ΔE Value as Fitting to Theoretical Convolution of Lorentzian Function

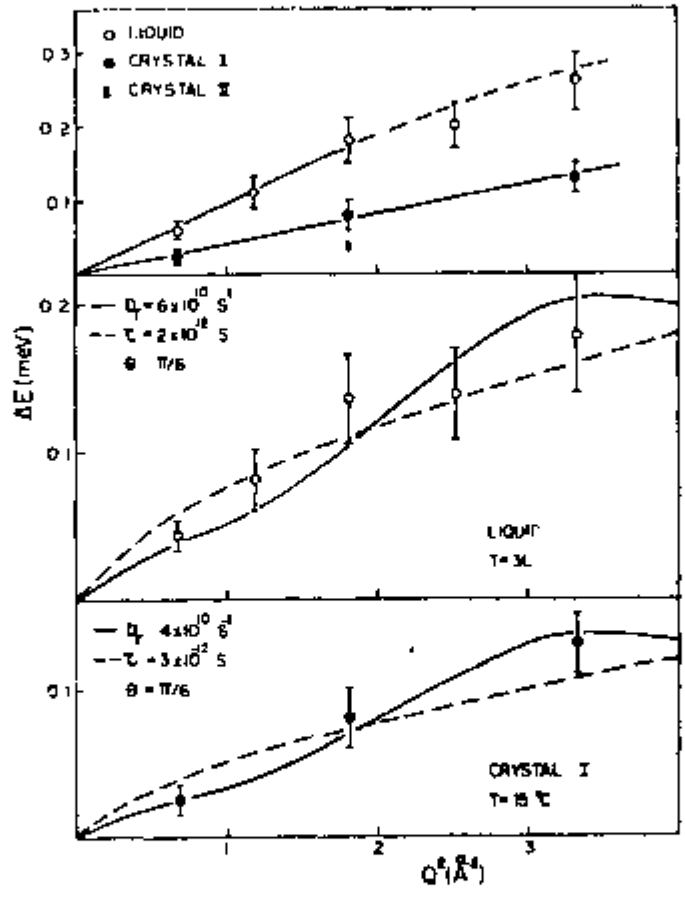

Figure 6 — Lorentzian Half Width ΔE of Quasielastic Scattering as a Function of Q^2. Linear Behavior for Low Q Values Analyzed According to Larsson's Model in the Upper Figure. Rotational Contributions for Liquid and Crystal I Analyzed According to Simple Rotational Diffusion Model (Solid Line) and Jump Diffusion Model (Dashed Line) in the Middle and Lower Figures.

The experimental Debye Waller factors indicate α^2 values much larger than the expected for translational motions of the whole molecule Assuming a Debye spectrum for the translational vibrations the relation $\alpha^2 = 3\hbar^2 T/Mk\theta^2$ gives a value $\alpha^2 \sim 0.06$ Å^2 for $\theta = 100$ K The internal methyl vibration could give a small contribution of $\alpha^2 \sim 0.03$ Å^2 estimated from the molecular geometry and the 31 meV torsional oscillation Thus the α^2 experimental values clearly indicate a contribution of the overall molecular rotation This means that the neutron is acutally seeing molecular librations[27] A libration with $M_0 = 3I/2d^2 = 26m$ where m is the proton mass and energy 5 meV would give $\alpha^2 \sim 0.17$ Å at 30°C that could explain the measured values Different rotational contributions seem to exist for the liquid and crystal I, but, the precision in α^2 values does not allow a more detailed analysis

The $\Delta E \times Q^2$ curve can be analyzed in terms of models for the molecular movements Firstly, an analysis will be made following Larsson's model[27] including rotational and translational diffusion, under the assumption that these two processes are uncorrelated In this model translation consists of alternate periods of vibration and simple diffusion while the movement around the center of mass consists of alternate periods of libration and rotational diffusion A linear behavior is espected for low Q^2 values according to

$$\Delta E = \hbar \left(D_{tr} + \frac{\langle r^2 \rangle + 2d^2}{6\tau} \right) Q^2$$

where D_{tr} is the macroscopic translational self-diffusion coefficient, $\langle r^2 \rangle$ is the mean square radius of the thermal could set up by the proton d is the proton distance to the center of mass, and τ is a correlation time for molecular rotations This behavior for low Q values is expected to be correct even in the case of bad resolution

The self diffusion translational coefficient was determined by Kessler[28] as $(3.7 \pm 0.4)\ 10^{-5}$ cm^2/sec at 30°C and $d = 2.51$ Å from structural data[9] Using the measured values of α^2 the slopes at the origin of Figure 6 give the correlation times shown in Table II

Table II

Rotational Diffusion Coefficient D_r and Correlation Time τ for Molecular Obtained from the Analysis of Neutron and NMR Results

	Liquid		Crystal I	
	$D_r(s^{-1})$	τ (s)	$D_r(s^{-1})$	τ (s)
Larsson s model		$(2.2 \pm 0.5) \times 10^{-12}$		$(3.6 \pm 0.5) \times 10^{-11}$
Simple rotational diffusion	$(6.0 \pm 0.5) \times 10^{10}$		$(4.0 \pm 0.5) \times 10^{10}$	
Jump rotational diffusion ($\theta = \Pi/6$)		$(2.0 \pm 0.5) \times 10^{-12}$		$(3.0 \pm 0.5) \times 10^{-12}$
NMR ($D_r = 1/6\tau$)	0.12×10^{10}	14×10^{-11}		

It is possible also to analyse the results in terms of models that take into account only molecular rotations if the translational contribution in the liquid satte is subtracted, assuming $\Delta E_{tr} = \hbar D_{tr} Q^2$. Two models will be considered: (i) Simple rotational diffusion. Egelstaff[29] gives a curve of $\Delta\omega/D_r$ as a function of Q^2d^2 where $\Delta\omega = \Delta E/\hbar$ and D_r is a rotational diffusion coefficient. This curve takes into account several terms of the expansion of the rotational scattering function what is necessary for comparison with the ΔE measured in this experiment. The best fit is shown in Figure 6 and the values of D_r are in Table II. (ii) Jump rotational diffusion. Leadbetter[30] gives a curve of $(\Delta\omega\tau)$ as a function of Q^2d^2 having as parameter the angle θ of an average jump. τ is the residence time of the molecule. A reasonable fit to the jump model is obtained only in the case of small angular displacements ($\theta = \Pi/6$) when the behavior of the curve approaches that of simple rotational diffusion. The best fit is shown in Figure 6 and the values are in Table II.

In order to discuss the parameters obtained from these models a comparison is made in Table II with NMR results[10] for the liquid state at 30°C that correspond to movements of the proton of the OH group.

Results of Figure 6 and Table II indicate that the jump diffusion model does not give the best fit to neutron data and is incompatible with NMR results. It is therefore concluded that although molecular librations must exist as evidenced by Debye Waller factors, jump rotational diffusion cannot account for the observed broadening. Simple rotational diffusion explain the observed ΔE but the D_r are much larger than NMR measurements. Besides this model cannot account for the obtained Debye Waller factors. Larsson's model explains neutron data but τ values are 6 times smaller than NMR results. The discrepancy between Larsson's model and simple rotational diffusion is due partially to the different dynamical model and partially to the approximations involved in the calculations. Therefore, although the uncertainties on the parameters are relatively small, only their order of magnitude are really meaningful.

To conciliate neutron data with NMR results it is proposed the existence of two different motions: individual molecular librations superposed to a cooperative rotational diffusion involving for instance trimers associated by H bonding known to exist in *tert* butanol[13]. Higher values of d would correspond to this cooperative rotational diffusion and smaller values of D_r has well as larger of τ would explain the measured ΔE. In Larsson's model for instance $d \sim 6.7$ Å would give the τ values measured by NMR; this result however cannot be used to estimate the correlation range since the model is not valid in the case of cooperative rotation. It is possible however, to conclude that cooperative rotation occurs both in crystal I and liquid phases.

Such a result is in agreement with Egelstaff's analysis of cooperative rotation in the plastic phase of cyclohexane[29] and with the fact that in general there is insufficient space for molecules to turn independently not only in the plastic crystal phase[31] but even in the liquid state[32]. It is, therefore suggested that NMR results obtained with the proton from the OH group refer actually to rotational diffusion of larger units kept together by H bonding between neighboring molecules. This would explain the high activation energies of 9 kcal/mol obtained[10] from NMR and viscosity data.

Results show also that there is rotational contribution present in the crystal II phase, that subsists below the transition temperature; this broadening is too small to be analyzed as a function of Q^2 and the possible contribution of CH_3 motions makes the analysis more difficult. The existence of this broadening in crystal II however indicates rotation of a quasispherical globule[33] in a situation where the amount of rotational energy increases steadily and not abruptly. As the *tert*-butanol molecule is not perfectly spherical and is bound to its neigbors by H bonding, the broadening in phase II indicates that a spherical globule of, for instance, three associated molecules, could be responsible for a rotational diffusion process. This explanation agrees with the analysis of ΔE for the other phases.

The general conclusion must be made that while cooperative rotational diffusion exists even in the crystal II phase, the solidlike behavior is evidenced by the inelastic spectra of the liquid state. Thus *tert* butanol exhibits both a strong order in the short range and rotational disorder in a long range. The

low entropy of melting must be due to ordering in the liquid maintained by H bonds as has been suggested also for other associated compounds[34] particularly methanol[35] Probably the motions of larger units are changing over state and phase transitions A more definite analysis of the molecular dynamics could be made only with the exact knowledge of the crystalline structures in the solid state, that have not yet been determined

RESUMO

A dinamica molecular do butanol terciário em duas fases cristalinas e no estado líquido foi investigada por meio do espalhamento de nêutrons frios no intervalo de temperatura de 8 a 35°C Os espectros de nêutrons espalhados inelasticamente apresentam essencialmente o mesmo comportamento evidenciando a existência de ordem a curto alcance no estado líquido

Um espectro de frequências obtido pela soma de sete gaussianas descreveu a distribuição em tempo de vôo medida e permitiu a assinalação das posições dos picos Foi obtida uma barreira $V_3 = (4.0 \pm 0.2)$ kcal/mol para a rotação interna do grupo CH_3 os resultados são compatíveis com um termo de segunda ordem $V_2 \simeq 0.1 V_1$ O alargamento da linha quase-elástica e os fatores de Debye-Waller foram analisados segundo vários modelos para a difusão molecular e os resultados foram comparados com aqueles obtidos por NMR Concluiu-se que a difusão rotacional cooperativa ocorre nos estados sólido e líquido

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