

Noack and Preissing lowest temperature $T_1(\omega)$ data (0—20°C) first, and then kept constant for higher temperatures. It is found that for values of $\alpha \leq 0.005$ the over-all error to the $T_1(\omega)$ data is <5% for all temperatures and is lowest (1%–3%) at the high temperatures. If values of $\alpha > 0.005$ are used the individual high frequency T_1 data points at the low temperatures do not fit within the estimated experimental error to the data ($\approx \pm 10\%$). Hence we have chosen $\alpha = 0.005$ as the limit to our fit and these results are used in the following discussion. It should be noted that according to the above analysis if $\alpha \rightarrow 0$ the asymptotic behavior of T_1 will lead to a frequency dependence $\approx \omega^{3/2}$ which is the reported experimental result of Noack and Preissing for the -10, -20°C $T_1(\omega)$ curves. Use of $\alpha = 0.005$ predicts a gradual curvature for T_1 [ω ; $\tau_t = \text{const}$]. This small curvature however is still consistent with the data within the relative error of the frequency data available.

Figure 7 presents the Noack and Preissing data, the solid lines represent the Torrey (Kruger) function generated for the correlation time τ_t and distances of closest approach d determined for best fit to the data at each temperature. The representation of the data is found to be very good over the entire range of measurement.

From the τ_t and d values produced by the fit, a value of the self-diffusion constant D can be generated for each temperature by using Eq. (10). The value of the D obtained from the fit can then be compared to actual experimental values³⁰ given in Fig. 8. The results of these calculations over this frequency and temperature range provide strong evidence of the validity of the Torrey translational diffusion model.

Referring to the choice of $A(\rho)$ in Sec. III.A of the

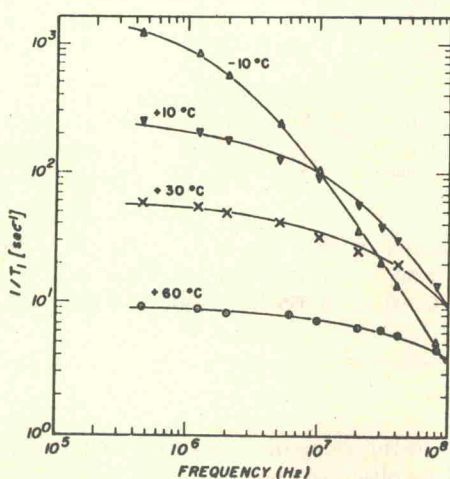


FIG. 7. Spin-lattice relaxation in glycerol as a function of frequency. The data points are taken from NP⁷. The solid lines represent the Torrey (Kruger) function generated for the correlation time τ_t and distances of closest approach d , determined from best fit reduction as discussed in the text.

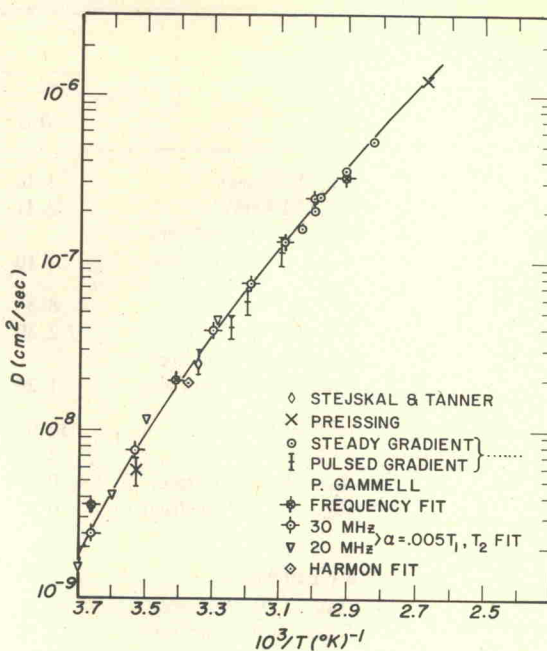


FIG. 8. Diffusion constant as a function of temperature at atmospheric pressure in glycerol; experimental and fitted values. See Ref. 30.

theory and substituting into Eq. (5), $\tau = (2\rho^2/D)^{-1}$, $\tau_0 = d^2/2D$ it can be shown that the $J_1(\omega)$ used by Noack and Preissing³¹ is proportional to the $J_{t,\alpha=0}(\omega)$ in the Torrey theory. The proportionality constant is $(2/5b^6)/(8\pi/15d^3)$. However, the ratio $T_1(\omega\tau_0)/T_1(0)$ which NP use to demonstrate their fit is independent of the rotational constant. Therefore the reasonable success of their frequency fit must also be regarded then as representing the usefulness of the translational model. Noack and Preissing's relatively poorer fit at low values of $\omega\tau_0$ (high temperature) probably is due to the fact that the d used in their procedure must be kept within certain bounds to be physically consistent with the hybrid interpretation of $J_t(\omega)$.

No restriction of d is made in our fits. Using the two parameter fitting procedure on τ_t and d described above, $T_1(\omega\tau_t)/T_1(0)$ can be produced as a function of $\omega\tau_t$ for the $\alpha=0$ limit to compare with the fit of Noack and Preissing; in this limit $\tau_t = d^2/5D$. The results are shown in Fig. 9 which can be compared to Noack and Preissing.⁷

The second method of reduction makes use of T_1 and T_2 temperature data at $\omega = \text{const}$ (30 MHz) and allows an independent check on the results of the frequency data reduction; and also provides a two parameter fit to the data. This T_1, T_2 reduction is used to analyze all the temperature and pressure data taken for glycerol, MPD and BUT. In this method the ratio of T_1/T_2 from translational theory is fitted to match the ratio of (T_1/T_2) data for each temperature (for each pres-

TABLE I. The reduced parameters: τ , translational correlation time; d , distance of closest approach; D_{calc} , translational

T (°C)		Glycerol ^a						
		0.0	0.5	1.0	1.5	2.0	2.5	3.0
60.2	τ ($\times 10^{-10}$ sec)	5.30			8.5	9.6	11.3	13.5
	d ($\times 10^{-8}$ cm)	2.41			2.29	2.27	2.28	2.31
	D_{calc} ($\times 10^{-7}$ cm ² /sec)				1.40	1.30	1.00	0.800
	D_{exptl} ($\times 10^{-7}$ cm ² /sec)	2.10						
49.4	τ ($\times 10^{-10}$ sec)	8.5	9.7	11.0	12.5	15.0	18.0	21.5
	d ($\times 10^{-8}$ cm)	2.30	2.22	2.22	2.18	2.16	2.15	2.17
	D_{calc} ($\times 10^{-7}$ cm ² /sec)		1.15	0.960	0.820	0.660	0.540	0.420
	D_{exptl} ($\times 10^{-7}$ cm ² /sec)	1.20						
39.3	τ ($\times 10^{-10}$ sec)	13.0	15.0	18.0	21.0	26.0	31.3	39.0
	d ($\times 10^{-8}$ cm)	2.18	2.12	2.10	2.08	2.05	2.03	2.03
	D_{calc} ($\times 10^{-7}$ cm ² /sec)	0.780	0.660	0.540	0.420	0.330	0.260	0.200
	D_{exptl} ($\times 10^{-7}$ cm ² /sec)	0.670						
30.0	τ ($\times 10^{-9}$ sec)	2.10	2.60	3.25	3.95	5.00	6.10	7.80
	d ($\times 10^{-8}$ cm)	2.07	2.02	2.00	1.97	1.95	1.92	1.91
	D_{calc} ($\times 10^{-8}$ cm ² /sec)	4.30	3.40	2.60	2.00	1.50	1.20	0.90
	D_{exptl} ($\times 10^{-8}$ cm ² /sec)	3.60						
21.0	τ ($\times 10^{-9}$ sec)	3.80	5.00	6.50	8.20	10.3	13.1	17.0
	d ($\times 10^{-8}$ cm)	1.97	1.93	1.90	1.88	1.86	1.83	1.80
	D_{calc} ($\times 10^{-8}$ cm ² /sec)	2.10	1.60	1.15	0.860	0.640	0.500	0.380
	D_{exptl} ($\times 10^{-8}$ cm ² /sec)	1.80						
12.6	τ ($\times 10^{-9}$ sec)	7.80	10.8	14.0	18.0	23.0	30.0	39.5
	d ($\times 10^{-8}$ cm)	1.98	1.85	1.82	1.81	1.79	1.76	1.73
	D_{calc} ($\times 10^{-8}$ cm ² /sec)	0.940	0.680	0.480	0.355	0.270	0.210	0.160
	D_{exptl} ($\times 10^{-8}$ cm ² /sec)	0.830						
4.6	τ ($\times 10^{-9}$ sec)	18.0	25.0	33.0	42.0	54.0	70.0	93.0
	d ($\times 10^{-8}$ cm)	1.82	1.79	1.76	1.75	1.73	1.71	1.67
	D_{calc} ($\times 10^{-8}$ cm ² /sec)	0.385	0.270	0.190	0.145	0.110	0.085	0.064
	D_{exptl} ($\times 10^{-8}$ cm ² /sec)							
-2.8	τ ($\times 10^{-8}$ sec)	4.30	5.90	7.90	10.0	13.0	16.6	22.0
	d ($\times 10^{-8}$ cm)	1.76	1.73	1.70	1.70	1.68	1.65	1.62
	D_{calc} ($\times 10^{-8}$ cm ² /sec)	0.150	0.105	0.074	0.058	0.048	0.033	0.025
	D_{exptl} ($\times 10^{-8}$ cm ² /sec)							
-10.0	τ ($\times 10^{-8}$ sec)	10.3	14.0	19.0	24.0	31.0	40.0	53.0
	d ($\times 10^{-8}$ cm)	1.70	1.68	1.64	1.65	1.63	1.60	1.58
	D_{calc} ($\times 10^{-9}$ cm ² /sec)	0.580	0.400	0.280	0.220	0.165	0.130	0.090
	D_{exptl} ($\times 10^{-9}$ cm ² /sec)							
-16.8	τ ($\times 10^{-8}$ sec)	24.0	33.0	44.0	58.0	74.0	94.0	120.0
	d ($\times 10^{-8}$ cm)	1.64	1.64	1.58	1.62	1.57	1.55	1.55
	D_{calc} ($\times 10^{-9}$ cm ² /sec)	0.225	0.150	0.100	0.086	0.060	0.048	0.034
	D_{exptl} ($\times 10^{-9}$ cm ² /sec)							

^a Data from graphs (Figs. 13, 14, 16).

sure). Since T_{1t}/T_{2t} from Eqs. (11) and (12) is only a function of τ_t , d is eliminated. This allows τ_t to be determined directly and then d is produced from the T_1 relationship [Eq. (11)]. As in the previous method, the value of α is kept constant for all temperatures. The values τ_t and d are then used to produce T_{2t} which is

compared to the value of T_2 experimentally measured. It should be observed that as the motional narrowing region is approached in these liquids at higher temperatures and lower pressure the ratio of T_1/T_2 approaches unity and the precision of the T_1 , T_2 fit calculation becomes increasingly poor. An example which indicates