

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 qme 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  $T_1$  [ $\omega$ ;  $\tau_t = \text{const}$ ]. 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  $\tau_t$  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  $\tau_t$  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 values<sup>30</sup> 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

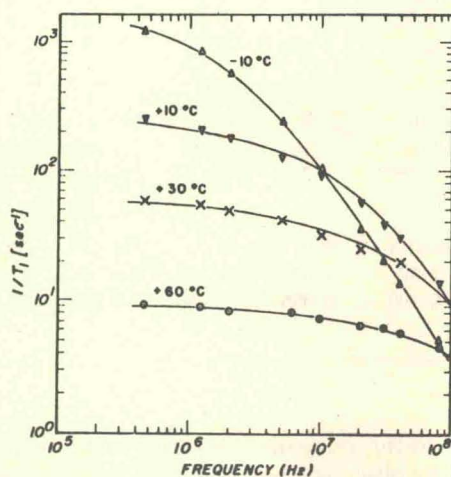


FIG. 7. Spin-lattice relaxation in glycerol as a function of frequency. The data points are taken from NP<sup>7</sup>. The solid lines represent the Torrey (Kruger) function generated for the correlation time  $\tau_t$  and distances of closest approach  $d$ , determined from best fit reduction as discussed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

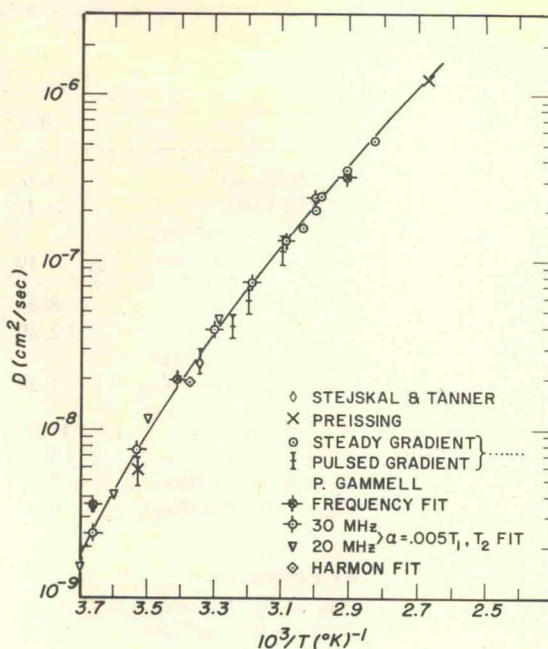


FIG. 8. Diffusion constant as a function of temperature at atmospheric pressure in glycerol; experimental and fitted values. See Ref. 30.

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 Preissing<sup>31</sup> 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  $\tau_t$  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.<sup>7</sup>

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  $T_{1t}/T_{2t}$  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:  $\tau$ , translational correlation time;  $d$ , distance of closest approach;  $D_{\text{calc}}$ , translational

| $T$ (°C) |   | Glycerol <sup>a</sup> |       |       |       |       |       |       |
|----------|---|-----------------------|-------|-------|-------|-------|-------|-------|
|          |   | 0.0                   | 0.5   | 1.0   | 1.5   | 2.0   | 2.5   | 3.0   |
| 60.2     | $\tau$ ( $\times 10^{-10}$ 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  |
|          | $D_{\text{calc}}$ ( $\times 10^{-7}$ cm <sup>2</sup> /sec)  |                       |       |       | 1.40  | 1.30  | 1.00  | 0.800 |
|          | $D_{\text{exptl}}$ ( $\times 10^{-7}$ cm <sup>2</sup> /sec) | 2.10                  |       |       |       |       |       |       |
| 49.4     | $\tau$ ( $\times 10^{-10}$ 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  |
|          | $D_{\text{calc}}$ ( $\times 10^{-7}$ cm <sup>2</sup> /sec)  |                       | 1.15  | 0.960 | 0.820 | 0.660 | 0.540 | 0.420 |
|          | $D_{\text{exptl}}$ ( $\times 10^{-7}$ cm <sup>2</sup> /sec) | 1.20                  |       |       |       |       |       |       |
| 39.3     | $\tau$ ( $\times 10^{-10}$ 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  |
|          | $D_{\text{calc}}$ ( $\times 10^{-7}$ cm <sup>2</sup> /sec)  | 0.780                 | 0.660 | 0.540 | 0.420 | 0.330 | 0.260 | 0.200 |
|          | $D_{\text{exptl}}$ ( $\times 10^{-7}$ cm <sup>2</sup> /sec) | 0.670                 |       |       |       |       |       |       |
| 30.0     | $\tau$ ( $\times 10^{-9}$ 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  |
|          | $D_{\text{calc}}$ ( $\times 10^{-8}$ cm <sup>2</sup> /sec)  | 4.30                  | 3.40  | 2.60  | 2.00  | 1.50  | 1.20  | 0.90  |
|          | $D_{\text{exptl}}$ ( $\times 10^{-8}$ cm <sup>2</sup> /sec) | 3.60                  |       |       |       |       |       |       |
| 21.0     | $\tau$ ( $\times 10^{-9}$ 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  |
|          | $D_{\text{calc}}$ ( $\times 10^{-8}$ cm <sup>2</sup> /sec)  | 2.10                  | 1.60  | 1.15  | 0.860 | 0.640 | 0.500 | 0.380 |
|          | $D_{\text{exptl}}$ ( $\times 10^{-8}$ cm <sup>2</sup> /sec) | 1.80                  |       |       |       |       |       |       |
| 12.6     | $\tau$ ( $\times 10^{-9}$ 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  |
|          | $D_{\text{calc}}$ ( $\times 10^{-8}$ cm <sup>2</sup> /sec)  | 0.940                 | 0.680 | 0.480 | 0.355 | 0.270 | 0.210 | 0.160 |
|          | $D_{\text{exptl}}$ ( $\times 10^{-8}$ cm <sup>2</sup> /sec) | 0.830                 |       |       |       |       |       |       |
| 4.6      | $\tau$ ( $\times 10^{-9}$ 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  |
|          | $D_{\text{calc}}$ ( $\times 10^{-8}$ cm <sup>2</sup> /sec)  | 0.385                 | 0.270 | 0.190 | 0.145 | 0.110 | 0.085 | 0.064 |
|          | $D_{\text{exptl}}$ ( $\times 10^{-8}$ cm <sup>2</sup> /sec) |                       |       |       |       |       |       |       |
| -2.8     | $\tau$ ( $\times 10^{-8}$ 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  |
|          | $D_{\text{calc}}$ ( $\times 10^{-8}$ cm <sup>2</sup> /sec)  | 0.150                 | 0.105 | 0.074 | 0.058 | 0.048 | 0.033 | 0.025 |
|          | $D_{\text{exptl}}$ ( $\times 10^{-8}$ cm <sup>2</sup> /sec) |                       |       |       |       |       |       |       |
| -10.0    | $\tau$ ( $\times 10^{-8}$ 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  |
|          | $D_{\text{calc}}$ ( $\times 10^{-9}$ cm <sup>2</sup> /sec)  | 0.580                 | 0.400 | 0.280 | 0.220 | 0.165 | 0.130 | 0.090 |
|          | $D_{\text{exptl}}$ ( $\times 10^{-9}$ cm <sup>2</sup> /sec) |                       |       |       |       |       |       |       |
| -16.8    | $\tau$ ( $\times 10^{-8}$ 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  |
|          | $D_{\text{calc}}$ ( $\times 10^{-9}$ cm <sup>2</sup> /sec)  | 0.225                 | 0.150 | 0.100 | 0.086 | 0.060 | 0.048 | 0.034 |
|          | $D_{\text{exptl}}$ ( $\times 10^{-9}$ cm <sup>2</sup> /sec) |                       |       |       |       |       |       |       |

<sup>a</sup> Data from graphs (Figs. 13, 14, 16).

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