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Neutron Inelastic Scattering Studies of Globular Compounds

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The use of neutron inelastic scattering measurements to determine the nature of the solid-state transitions in globular compounds is proposed and exemplified. Patterns were taken of the high- and low-temperature phases of solid cyclohexane, 2-2-dimethylbutane, and 1-4-diazo-bicyclo-(2.2.2)-octane. The first two have broad inelastic scattering peaks in the low-temperature phase. In the high-temperature phase these peaks disappear and the elastic peak broadens markedly. These changes are attributed to "quasi-free-rotation" of the molecules. Inelastic peaks do not appear in 1-4-diazo-bicyclo-(2.2.2)-octane, and the elastic peak does not broaden appreciably in the high-temperature phase. Self-diffusion coefficients $D_s=4.5\times 10^{-6}$ cm²/sec for cyclohexane and $D_s=8.6\times 10^{-6}$ cm²/sec for 2-2-dimethylbutane were determined from the patterns of the liquids at 300°K using the "small motions" approximation. These values are larger than those obtained from NMR measurements, presumably as a result of irreversible rotation of the molecules.

MANY globular compounds¹ are characterized by relatively high melting points, high vapor pressures, first-order transitions with large entropy changes in the solid state, and a certain degree of plasticity in the high-temperature phase. The phase transitions are from a low-temperature ordered phase, to a highly disordered high-temperature phase. The nature of the transition has been studied by x-ray diffraction,² nuclear magnetic resonance³ (hereafter NMR), calorimetry,⁴ and by means of measurements of dielectric constants in polar molecules.⁵ Of these methods x-ray diffraction and calorimetry cannot distinguish clearly between a passage to a dynamically disordered phase (molecules reorienting almost freely) or to a statistically disordered phase (molecules in different but fixed orientations in different cells). The existence of rotations in the solid can be detected by NMR since it will narrow the linewidth and reduce the second moment of the line. Also, measurements of spin-lattice relaxation times give reorientation rates. Polar molecules with freedom to reorient will give high dielectric constants, so that here also we have a method for establishing the existence of rotation in the solid.

In addition to the above mentioned methods, there exists the possibility of detecting the existence of "quasi-free-rotation" in the solid by the use of neutron inelastic-scattering experiments.⁶ If the intermolecular

forces opposing rotation in the solid are very weak and a large proportion of molecules are able to surmount this potential barrier, the neutron-scattering pattern should show a very broad peak, centered near the elastic peak, whose width diminishes markedly with decreasing Q (momentum transfer in units of \hbar). Furthermore, if there are inelastic scattering peaks due to modes of intermolecular vibrations in the low-temperature phase, they should disappear above the transition temperature, i.e., they will move to the region of almost zero energy transfer. The work described in this paper was done to demonstrate the foregoing statements, establishing at the same time the nature of the disorder in some globular compounds. Experiments were also made on these substances in the liquid state. Since the intermolecular forces in some of them should be similar to those in the inert gases, presenting experimental advantages over the latter (ease of handling, highly incoherent scattering), it is considered that a study of them should be rewarding in order to elucidate the structural dynamics of liquids. The work described here on liquids is only illustrative.

The substances studied were cyclohexane, 2-2-dimethylbutane and 1-4-diazo-bicyclo-(2.2.2)-octane (hereafter DABCO) in the solid state. The first two were also studied in the liquid state. Cyclohexane has an fcc crystal structure in the high-temperature phase and its x-ray diffraction pattern shows evidence of disorder.⁷ There is a first-order phase change at 186°K below which the crystal symmetry is perhaps monoclinic.⁸ NMR studies show that there is almost isotropic reorientation of the molecules at a rate of at

¹ J. Timmermans, *Phys. Chem. Solids* **18**, 1 (1961).

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² W. J. Dunning, *Phys. Chem. Solids* **18**, 21 (1961).

³ E. R. Andrew, *Phys. Chem. Solids* **18**, 9 (1961).

⁴ K. A. L. Staveley, *Phys. Chem. Solids* **18**, 46 (1961).

⁵ C. P. Smyth, *Phys. Chem. Solids* **18**, 40 (1961).

⁶ B. N. Brookhouse, *Inelastic Scattering of Neutrons in Solid and Liquids* (I.A.E.A., Vienna, 1961), p. 113.

⁷ T. Oda, *X-Sen* **5**, 26 (1948) (C.A. **44**, 5179d).

⁸ G. S. Krishna Murthi, *Indian J. Phys.* **32**, 460 (1958).

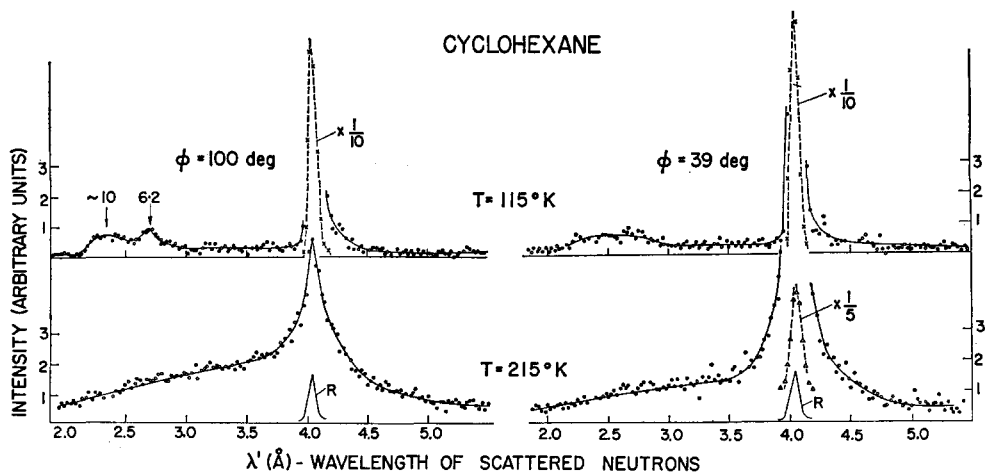


FIG. 1. Plot of intensity vs scattered-neutron wavelength of cyclohexane powder at 115° and 215°K, and scattering angles of 39° and 100°. The position of the peaks are given in meV.

east 10^6 cps above 186°K.⁹ Also 2-2-dimethylbutane has fcc crystal structure in the high-temperature phase¹⁰ and has a first-order transition at 127°K. Its behavior as studied by NMR is similar to that of cyclohexane and can also be explained by the existence of almost isotropic reorientation above 127°K. DABCO undergoes a first-order solid-state transition at 80°C, as determined by calorimetric measurements.^{11,12} To

our knowledge no NMR work has been done on DABCO, and very little x-ray work has been done.¹³

The neutron inelastic-scattering experiments were done with the Chalk River rotating crystal spectrometer.⁶ Neutrons of incident wavelength 4.059 Å were scattered from very thin specimens (0.5 mm thickness) at scattering angles ϕ of 19°, 39°, and 100° (corresponding to Q 's of 0.518, 1.050, and 2.400 Å⁻¹, respec-

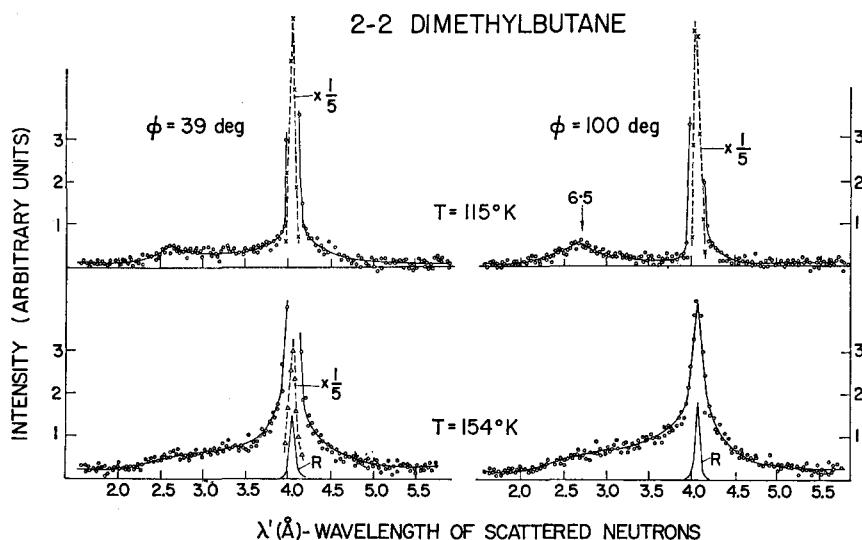


FIG. 2. Plot of intensity vs scattered-neutron wavelength of 2-2-dimethylbutane at 115° and 154°K, and scattering angles 39° and 100°. The position of the peak is given in meV.

⁹ E. R. Andrew and R. G. Eades, Proc. Roy. Soc. (London) **A216**, 398 (1953).

¹⁰ B. Post, R. S. Schwartz, and I. Fankuchen, J. Am. Chem. Soc. **73**, 5113 (1951).

¹¹ S. S. Chang and E. F. Westrum, Jr., J. Phys. Chem. **64**, 1551 (1960).

¹² E. F. Westrum, Phys. and Chem. Solids **18**, 83 (1961).

¹³ S. Saki (unpublished work); see reference 12.

tively) for liquid cyclohexane and liquid 2-2-dimethylbutane, and at angles of 39° and 100° for the solids above and below the transition points. Studies of solid DABCO were made only at $\phi = 100^\circ$, above and below the transition point. The times of flight of the scattered neutrons with energies near the incident energy were measured in a 178-channel time sorter. For each specimen the net counting rate N_0 was normalized utilizing:

$$N_0 = [(N - N_{cd})_s / M_s] - T[(N - N_{cd})_b / M_b],$$

where T is the transmission of the specimen, N_s and M_s the monitor counts for measurements with and without specimen, referred to by the subscripts s and b , respectively, and N_{cd} refers to measurements made with cadmium in the beam. The transmission in the

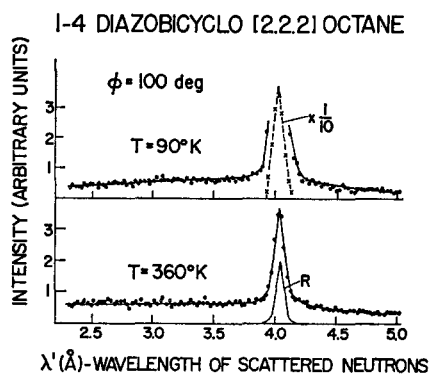


FIG. 3. Plot of intensity vs scattered-neutron wavelength of 1-4-diazobicyclo-(2.2.2)-octane at 90° and 360°K , and scattering angle of 100° .

forward direction, at 300°K , was measured before and after the whole series of patterns for each substance was taken, the values obtained are: $T(\text{cyclohexane}) = 78\%$; $T(2\text{-}2\text{-dimethylbutane}) = 88\%$ and $T(\text{DABCO}) = 75\%$. The normalized counting rates, after correction for counter efficiency, are shown in Figs. 1–5. The patterns for each substance are normalized together, so intensities can be directly compared for each one of them. These figures also show the resolution function (R) for each Q , obtained from a series of measured distributions of the elastic incoherent scattering by vanadium metal.

The elastic peaks of solid cyclohexane and 2-2-dimethylbutane show appreciable broadening in passing from the low-temperature to the high-temperature phase. This can be seen very clearly in Figs. 1–2, the difference at the low-temperature being quite drastic. Also, the reduction in width with decreasing Q of the elastic peak of these substances is very marked in the high-temperature phase. This behavior of the diffrac-

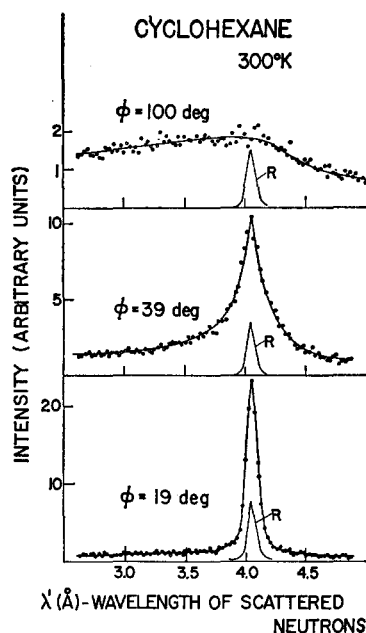


FIG. 4. Plot of intensity vs scattered-neutron wavelength of liquid cyclohexane at 300°K , and scattering angles of 19° , 39° and 100° .

tion pattern can be attributed to the existence of “quasi-free-rotation.” The broad inelastic peaks observed in the low-temperature phase, corresponding to energy transfer ($\hbar\omega$) of 6.5 meV in 2-2-dimethylbutane and to 6.2 and 10 meV in cyclohexane are probably due to modes of intermolecular vibration. Their disappearance in the high-temperature phase and the broadening of the elastic peak lead to the conclusion that the high-temperature phases of cyclohexane and

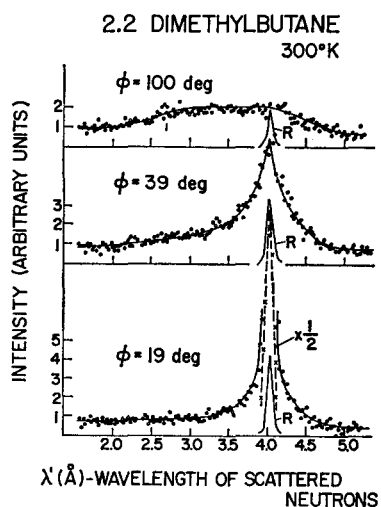


FIG. 5. Plot of intensity vs scattered-neutron wavelength of liquid 2-2-dimethylbutane at 300°K , and scattering angles of 19° , 39° , and 100° .

2-2-dimethylbutane are dynamically disordered. No evidence of this can be observed in DABCO, the patterns at two temperatures shown in Fig. 3 are of almost identical shape.

Figures 4 and 5 show the diffraction patterns for liquid cyclohexane and liquid 2-2-dimethylbutane at 300°K. In all patterns the diffusive broadening of the quasi-elastic peak was observed.¹⁴ Values of the coefficients of self-diffusion D_s were calculated on the assumption of a small motions mechanism by which $D_s = W/2Q^2$,¹⁴ where W is full width at half-maximum in units of \hbar of the quasi-elastic peaks. Assuming that the quasi-elastic peaks are Gaussian (in fact they are approximately Lorentzian), W was measured after correcting for resolution (the shape of the resolution function is approximately Gaussian). The following values of D_s were obtained: $D_s(\text{cyclohexane}) = 4.5 \times$

10^{-5} cm²/sec and $D_s(2\text{-}2\text{-dimethylbutane}) = 8.6 \times 10^{-5}$ cm²/sec, both from the pattern at $\phi = 39^\circ$. From NMR measurements of spin-lattice relaxation times the following values of D_s were obtained: $D_s(\text{cyclohexane}) = 1.38 \times 10^{-5}$ cm²/sec¹⁵ and $D_s(2\text{-}2\text{-dimethylbutane}) = 3.41 \times 10^{-5}$ cm²/sec,¹⁶ both at 25°C. The discrepancy between the D_s values from NMR and these obtained here must be mostly due to the effect of the irreversible rotations of the molecules.

ACKNOWLEDGMENTS

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¹⁵ D. W. McCall, D. C. Douglass, and E. W. Andrews, *J. Chem. Phys.* **31**, 1555 (1959).

¹⁶ D. C. Douglass and D. W. McCall, *Phys. Fluids* **2**, 87 (1959).

¹⁴ B. N. Brockhouse, *Suppl. Nuovo Cimento* **9**, 45 (1958).

Revised Tables for Ion-Exchange Kinetics

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(Received 22 October 1962)

Revised numerical solutions of the differential equation for exchange of ions of equal valence and different mobilities are presented for finite slabs and spherical particles under simple initial and boundary conditions. The solutions also apply to sorption and desorption with a particular concentration dependence of the diffusion coefficient. The relations with solutions given by others for semi-infinite media are discussed.

NUMERICAL solutions of the diffusion equation for ion-exchange kinetics have been given previously.^{1,2} These solutions have now been recalculated with a more accurate computer program. The results are given in Tables I and II.

SYMBOLS

a = constant parameter in Eq. (2)
 C = concentration
 C_A = concentration of counterion A in ion exchange
 C_0 = initial or boundary concentration
 D = diffusion coefficient, indices A and B refer to individual diffusion coefficients of counterions A and B in ion exchange

D_0 = diffusion coefficient at zero concentration
 k = constant in Eq. (5)
 r = radial space coordinate in spheres
 r_0 = sphere radius
 t = time
 x = space coordinate normal to surface in finite slabs
 x_0 = thickness of finite slab
 τ = dimensionless time

The tables list solutions of the diffusion equation,

$$\partial C / \partial t = \text{div}(D \text{ grad } C), \quad (1)$$

with a concentration-dependent diffusion coefficient,

$$D = D_0 [1 / (1 + aC/C_0)], \quad (2)$$

for various values of the parameter a and with the

¹ F. Helfferich and M. S. Plesset, *J. Chem. Phys.* **28**, 418 (1958).

² F. Helfferich, *J. Phys. Chem.* **66**, 39 (1962).