

Pressure dependence of the self-diffusion in liquid trifluoromethane

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A simple modification of a high resolution N.M.R. spectrometer is presented, permitting determination of self-diffusion coefficients at pressures up to 200 MPa in the temperature range between 140 K and 450 K. The self-diffusion coefficients of CHF_3 are determined between 142 K and 250 K. The activation energies derived from the data are $[E_a^D]_{p=\text{const}} = (6.1 \pm 0.4) \text{ kJ mol}^{-1}$, $[E_a^D]_{v=\text{const}} = (3.5 \pm 0.4) \text{ kJ mol}^{-1}$. Except for the lowest temperatures, compressed CHF_3 appears to behave as a normal, rough hard-sphere fluid.

1. INTRODUCTION

The single-particle dynamics of simple liquids can be derived from the investigation of the magnetic relaxation of the nuclear spins. However, the experiments give the spin-lattice- or spin-spin-relaxation rates at most at a few frequencies and one must thus rely on models or theories that connect the experimental data with the spectral density function. This fact is especially aggravating in low molecular weight, low viscosity liquids, since here the extreme narrowing limit condition applies and almost all relaxation mechanisms become independent of field and frequency [1, 2].

The self-diffusion coefficient D is the only dynamic quantity, characterizing single-particle motion, that can be obtained directly from experiments without recourse to any model assumptions. Among the various methods used to determine the self-diffusion coefficient of a liquid, magnetic spin echo experiments in a steady or pulsed field gradient have become the method of choice. In the following a simple modification of a standard high resolution spectrometer is described, that permits the determination of self-diffusion coefficients between 150 K and 450 K and at pressures up to 200 MPa. In a first series of experiments with this apparatus the self-diffusion coefficient of liquid trifluoromethane has been determined. In recent theories of simple liquids [3-5] arguments have been put forward that in the absence of strong, anisotropic attractive interactions, like hydrogen bonds, the structure and dynamics of these liquids is dominated by short-ranged repulsive interactions. Thus the concept of the hard-sphere fluid as a zeroth order approximation to real liquids has been developed. Within this approximation, expressions for the self-diffusion coefficient have been established by forcing the density dependence to fit molecular dynamics calculations of the hard sphere fluid [6]. The self

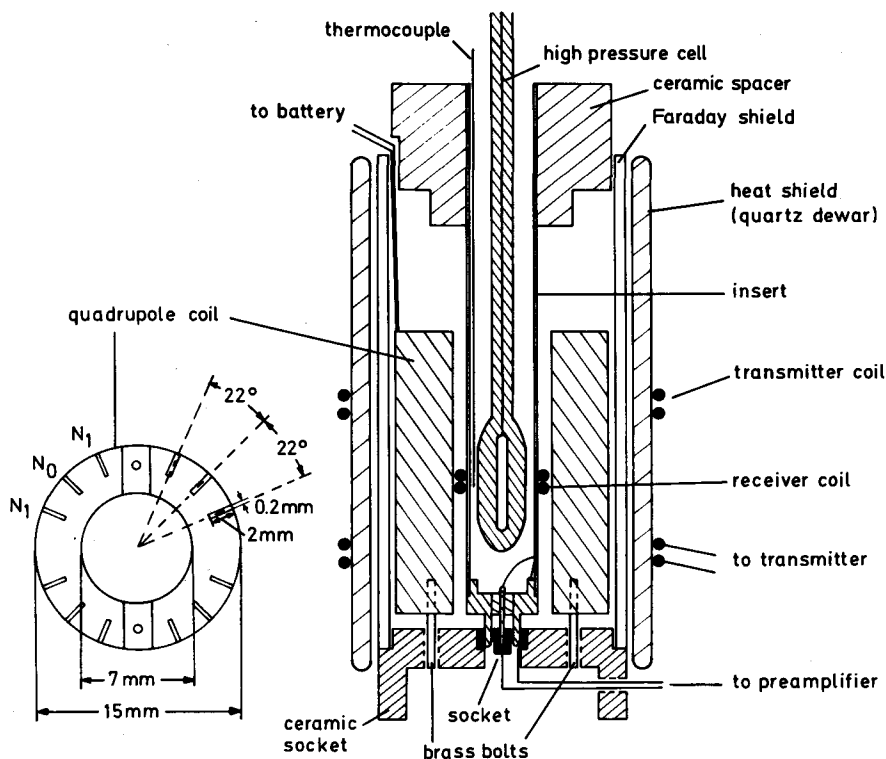


Figure 1. View of the variable-temperature, high-pressure device mounted in the standard Varian V 4415 probe. Left: Cross section of the gradient coil (Material: Macor glass ceramics).

diffusion coefficient of CHF_3 as function of density are discussed within the framework of the hard sphere model for non-associated molecular liquids.

2. EXPERIMENTAL

The self-diffusion coefficients D were determined in a Varian XL-100-15 FT spectrometer. Figure 1 gives a cross-section through the modified V-4415 probe. It was decided to use a quadrupole coil for the generation of the field gradients since this coil provides, compared with Helmholtz coils, larger horizontal gradients combined with a high gradient homogeneity along the vertical axis [7]. In addition it avoids magnetic-imaging problems and possesses a low inductivity only. The coil was fixed in the ceramic foot of the probe by two brass bolts. In order to minimize the effects of thermal expansion upon the coil geometry, the body of the coil was machined from glass ceramics (Macor, P. Schröder & Co., 2086 Ellerau, F.R. Germany).

Each quadrant of the coil contains three groups of windings of insulated 0.1 mm copper wire ($N_0=14$ turns, $N_1=10$ turns). The current for the coil was provided by a battery and regulated with a potentiometer. It was controlled by a digital amperemeter with an accuracy of ± 0.05 mA. The receiver coil is mounted on a thin-walled, ground quartz tube with an i.d. of 5.3 mm. The limited space available within this insert prohibits the use of a burst protection

around the high pressure glass cell. This cell was drawn from standard 5 mm o.d., 0.8 mm i.d. Duran 50 glass capillaries (Schott, Darmstadt, F.R. Germany). Details of the whole high pressure set-up, which is a modification of the strengthened glass-cell-design proposed by Yamada [8] have been given previously [9, 10].

The pressure was measured with a Bourdon gauge (Heise, Connecticut, U.S.A.) to ± 0.5 MPa. The temperature was regulated with the modified Varian variable temperatures accessory and controlled before and after each measurement by a miniature thermocouple (Philips, Kassel, F.R. Germany). The temperature could be kept constant to ± 0.5 K at any spot of the probe, however the introduction of the gradient coil partly obstructs the flow of the nitrogen gas used for thermostating and thus a small temperature gradient is established along the probe, leading to an overall temperature uncertainty of ± 1.5 K. The spin echo was obtained with a 90° - 180° pulse sequence. In the presence of a permanent field gradient the amplitude M^+ of the echo is given by

$$M^+(2\tau) = M_0 \exp[-2\tau/T_2] \exp[-D(\gamma G)^2 2\tau^3/3], \quad (1)$$

with τ the interval between the 90° and 180° pulse, T_2 the spin-spin-relaxation time, D the self-diffusion coefficient, γ the gyromagnetic ratio of the nucleus studied and G the magnetic field gradient ($G = kI$, $k = \text{coil constant}$). D can be derived either from a series of echoes obtained at constant G under variation of τ or at constant τ by applying an increasing gradient.

It appeared preferable to use the second alternative and work at constant τ . The gradient G was calibrated by determining the spin echoes of a neat oxygen free, water sample, for which the self-diffusion coefficient is well known [11]. The calibration was performed between 277 K and 368 K. The coil constant k is independent of temperature in this interval. During the course of the experiments several coils were applied for which k varied from 0.70 ± 0.01 to 0.90 ± 0.01 ($\text{Tm}^{-1} \text{A}^{-1}$). Since the coil constant depends on the exact alignment of the coil in the B_0 -field, the calibration is regularly repeated, before any measurements are started.

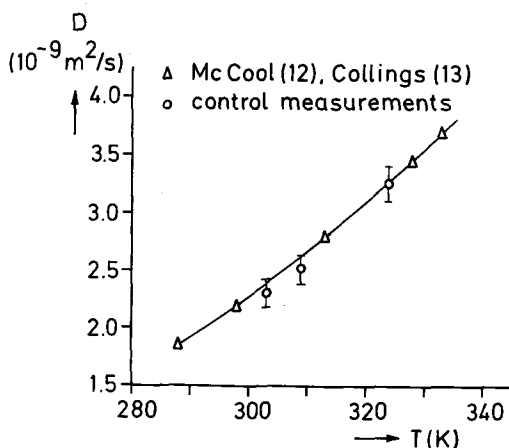


Figure 2. Comparison of the control measurements of the self-diffusion coefficient of liquid benzene with data from the literature.

The spin echoes are accumulated in the memory of the computer and are rectified before plotting. The amplitude of the signal as function of the gradient coil current $A(I)$ is registered and from a plot of $\log A$ versus I^2 the self-diffusion coefficient D is determined. The calibration of the set-up was controlled by measuring the ambient pressure self-diffusion coefficient of benzene. Figure 2 compares the published data [12, 13] for this substance with our experiments.

Trifluoromethane was purchased from Baker Chemikalien (6080 Groß-Gerau, F.R. Germany). It was dried over molecular sieve 3 Å and stored in a 5 l glass flask. Prior to use it was degassed by at least 5 freeze-pump-thaw-cycles to a final pressure of 5×10^{-3} Pa. Details of the filling procedure for the high pressure cell and the high vacuum apparatus used have been published previously [14]. All self-diffusion coefficients are judged reliable to ± 10 per cent.

3. RESULTS AND DISCUSSION

The self-diffusion coefficients D determined are compiled in table 1. In the literature only a few self-diffusion coefficients of CHF_3 at saturation pressure between 113 K and 173 K [15] could be found. These coefficients are approximately $2\frac{1}{2}$ times larger than our results. This difference must remain unexplained, since the samples have been cleaned carefully in both cases, as can

Table 1. Self-diffusion coefficients D ($10^{-9} \text{ m}^2 \text{ s}^{-1}$) for liquid CHF_3 .

Saturation pressure									
$T(\text{K})$	144	158	187	216	243				
D	0.88	1.4	2.7	4.9	7.1				
$p = 10 \text{ MPa}$									
$T(\text{K})$	147	161	182	205	246				
D	0.93	1.5	2.4	4.9	7.4				
$p = 50 \text{ MPa}$									
$T(\text{K})$	142	147	159	161	168	182	195	205	246
D	0.72	0.81	1.1	1.1	1.5	2.1	2.7	3.7	6.1
$p = 100 \text{ MPa}$									
$T(\text{K})$	142	147	160	161	168	205	224	243	246
D	0.52	0.61	0.78	0.86	1.1	2.1	2.8	3.5	4.9
$p = 150 \text{ MPa}$									
$T(\text{K})$	144	166	173	184	194	204	250		
D	0.44	0.84	0.93	1.4	1.5	1.9	4.0		
$p = 200 \text{ MPa}$									
$T(\text{K})$	166	184	204	255					
D	0.60	1.1	1.7	2.2					

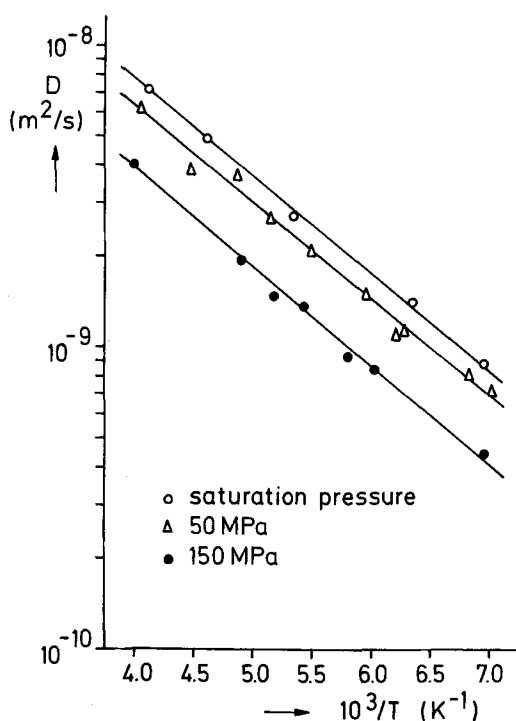


Figure 3. Temperature dependence of the self-diffusion coefficient of liquid CHF_3 at saturation pressure and at 50 and 150 MPa.

be deduced from the identical ^{19}F and ^1H spin lattice relaxation times [15, 22]. Thus the only plausible explanation for the difference could be convection of the CHF_3 caused by a temperature gradient or an error in the determination of the steady field gradient.

The isobars between saturation pressure and 200 MPa are within the limits of error straight lines with identical slopes. Figure 3 gives three of these isobars. The data at intermediate pressures have been omitted from the graph for the sake of clarity. A compact and convenient way to express experimental results is to calculate activation energies ΔE^\ddagger and activation volumes ΔV^\ddagger as a means to compare the pressure and temperature dependence of dynamic properties of different systems. This analysis is meaningful as long as an Arrhenius behaviour is found for the property under consideration although the underlying physical concept of an activated state may be questionable. From these isobars the activation energy at constant pressure can be calculated :

$$(\Delta E^\ddagger)_{p=\text{const}} := -R \left(\frac{\partial \ln D}{\partial \frac{1}{T}} \right)_p = (6.1 \pm 0.4) \text{ kJ mol}^{-1}.$$

From the isobars five isotherms have been constructed. These are shown in figure 4. The data at 188 K, 208 K and 250 K do show a pronounced curvature, the slope decreasing with increasing pressure, while the isotherms at

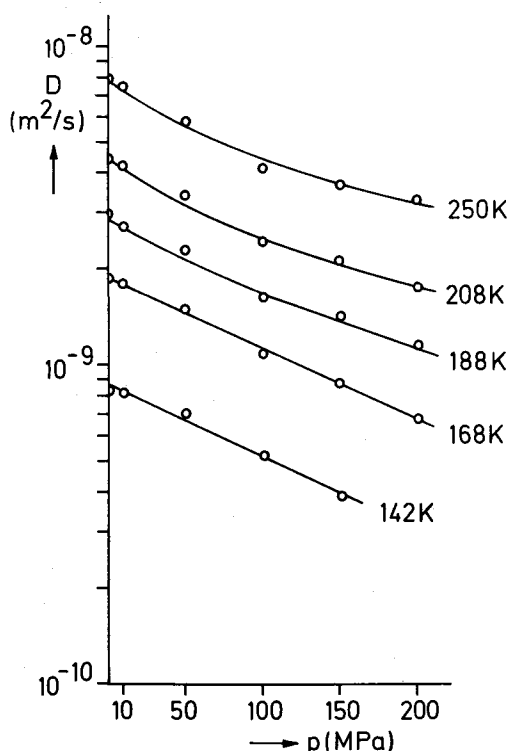


Figure 4. Pressure dependence of the self-diffusion coefficient D of liquid CHF_3 .

Table 2. Activation volumes for the self-diffusion in CHF_3 at saturation pressure and at 200 MPa.

$T(\text{K})$	142	168	188	208	250
$\Delta V_{\text{s.p.}}$ ($10^{-6} \text{ m}^3 \text{ mol}^{-1}$)			9.2 ± 1.0	13 ± 1.5	18 ± 2.0
$\Delta V_{200 \text{ MPa}}$ ($10^{-6} \text{ m}^3 \text{ mol}^{-1}$)	6.2 ± 1.0	7.1 ± 1.0	5.8 ± 1.0	5.5 ± 1.0	5.4 ± 1.0

142 K and 168 K are linear in the $\log D$ versus p presentation. From the slopes of the isotherms (figure 4) the activation volume for self-diffusion is derived :

$$\Delta V^\ddagger := -RT \left(\frac{\partial \ln D}{\partial p} \right)_T.$$

The data obtained at saturation pressure and at 200 MPa are compiled in table 2.

The isotherms of the $\log D$ versus pressure representation of figure 4 yield only a qualitative impression about the density dependence of the self-diffusion coefficient in CHF_3 . For a separation of the effects of the thermal energy

from the density variation one needs pVT data of the compound. Experimental data for the temperature and pressure region covered by our experiments are lacking. Kruse [16] correlated existing data on CHClF_2 and CHF_3 [17, 18] and gives extrapolated densities in the pressure range up to 300 MPa at temperatures between 300 K and 500 K. Gallant [19] gives data for the liquid density of CHF_3 at saturation pressure down to 150 K. Densities extrapolated graphically from the data given by Kruse [16] yield within ± 2 per cent the same densities as given by Gallant [19]. We therefore consider our crudely interpolated densities reliable to ± 4 per cent.

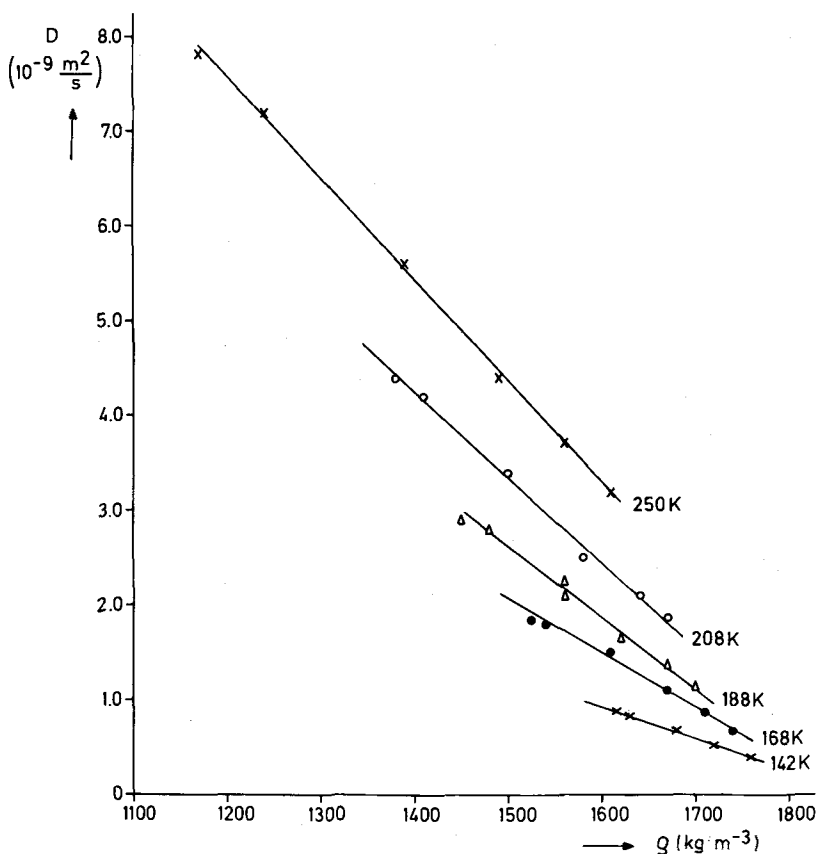


Figure 5. Density dependence of the self-diffusion coefficient D of liquid CHF_3 .

Figure 5 contains the isothermal density dependence of the self-diffusion coefficient. The points given in the diagram are taken from figure 4. A linear density dependence is found with a slope increasing with rising temperature. From an Arrhenius plot of the isochores for $1400 \leq \rho \leq 1700$ (kg m^{-3}), which are within the accuracy of the data linear with identical slopes, an activation energy at constant volume: $(E_a^D)_{V=\text{const}} = (3.5 \pm 0.4) \text{ kJ mol}^{-1}$ is calculated. The ratio of the two activation energies $(E_a)_p / (E_a)_V$ at constant pressure and at constant volume is close to 0.5 indicating that liquid CHF_3 behaves like a normal simple liquid [20]. For hydrogen bonded liquids like water or ammonia [21] these two activation energies are approximately the same.

The dynamics of simple liquids, composed of nearly spherical molecules, interacting mainly via short-ranged repulsive forces, are often well described by the corrected Enskog [23] theory as introduced by Dymond [3]. The self-diffusion coefficient of the smooth hard-sphere fluid D_{shs} is given in terms of the packing fraction ρd^3 of the liquid as [3–5]

$$D_{\text{shs}} = \frac{3}{8} \left(\frac{kT}{m\pi} \right)^{1/2} dP(\rho d^3) \quad (2)$$

with m the molecular mass, d the hard-sphere diameter, ρ the number density and $P(\rho d^3)$ an empirical polynomial in the packing fraction ρd^3 used to interpolate the molecular dynamics results of the hard-sphere fluid as obtained by Alder *et al.* [6]. In rough hard-sphere fluids or molecular liquids composed of particles with a non-spherical shape, rotation–translation coupling can occur with the effect of lowering the diffusion coefficient from what one would find in its absence. Chandler [4, 25, 26] has argued that this phenomenon can be taken into account by setting

$$D \simeq D_{\text{rhs}} = AD_{\text{shs}}, \quad (3)$$

where D is the self-diffusion coefficient of the molecular liquid, D_{rhs} and D_{shs} is the diffusion coefficient of the rough and smooth hard sphere fluid at the same packing fraction ρd^3 and the parameter A measures the degree of rotation–translation coupling. Dymond [3], Trappeniers [5] and Chandler [4] use different interpolation formulae to represent the density dependence of diffusion coefficients of the hard-sphere fluid. As the hard-sphere diameter is not known *a priori*, equation (2) is normally used together with the measured isothermal density dependence of the self-diffusion coefficient to estimate the hard-sphere diameter from the slope $(\partial \ln D / \partial \ln \rho)_T$ which can be compared to $\partial \ln D_{\text{shs}} / \partial \ln (\rho d^3)$. Note that the latter quantity is a function of the packing fraction only. For the density range $0.55 < (\rho d^3) < 0.95$ covered by our experiments all three equations (3)–(5) yielded nearly identical hard-sphere diameters as calculated from the isotherms of figure 5. They are collected in table 3. They show a weak temperature dependence with a decreasing hard-sphere diameter with increasing temperature due to the higher kinetic energy of the particles. With the hard-sphere diameter thus obtained the coupling parameter A can be obtained from equation (3). It is also given in table 3. A noticeable feature is the temperature dependence of the slope of $(\partial D / \partial \rho)_T$ which should be $\sim \sqrt{T}$ as predicted by theory (see (3)). In most liquids, however, a stronger

Table 3. Hard-sphere diameters d and A -parameter ($A = D_{\text{shs}} D_{\text{exp}}^{-1}$) of liquid CHF_3 derived from the data given in figure 4.

$T(\text{K})$	$d(\text{nm})$	A
142	0.396	0.38
168	0.398	0.57
188	0.399	0.65
208	0.390	0.60
250	0.378	0.59

increase with temperature of the slope in the D versus ρ plot is found. This has been interpreted to mean that the rotation-translation coupling factor is temperature dependent [24]. Considering the experimental errors no variation of A with temperature is seen except for the lowest temperature of 142 K. At the higher temperatures, the coupling parameter A is close to the value found for carbontetrachloride [4] ($A = 0.54$), which appears to be a typical example of a rough hard sphere fluid. The decrease at 142 K could indicate, that at low temperatures the dipole moment of CHF_3 of 1.65 D leads to more effective coupling of translation and rotation of the single molecule and thus to a temperature dependent coupling factor. However, the deviation can also be ascribed to the influence of the attractive part of the intermolecular potential at lower temperatures [27, 28].

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