Self Diffusion in Compressed Fluid CF_3Br and CF_3Cl

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Self diffusion coefficients of CF_3Br and CF_3Cl are given for the temperature range 140–430 K at pressures up to 200 MPa. The are analysed by the interacting sphere model.

Introduction

The correct description of the density and temperature dependence of the self diffusion coefficient D in a neat liquid is a crucial test for all physical theories aiming at a quantitative representation of the molecular dynamics in a wide ϱ, T range. Among the models proposed in the literature modifications of hard sphere treatments proved to be most successful [1–4].

Compared to smooth sphere self diffusion data obtained from molecular dynamics simulations, the self diffusion coefficients of real liquids, consisting of rigid halomethanes, are reduced. The reduction is increasing with falling temperature. Recently Speedy [5] proposed that these reductions are caused predominantly by attractive interactions between the molecules and not by rotation-translation coupling originating from the deviation of the individual molecules from spherical symmetry [1, 2]. In the following the data for CF_3Br and CF_3Cl, two moderately polar symmetric top molecules, are presented and analyzed in the framework of the hard sphere theories.

Experimental

Bromotrifluoromethane (99%) and Chlorotrifluoromethane (99%) were purchased from J. T. Baker (6080 Groß Gerau, FRG). Residual moisture was removed by passing the compressed gases through a stainless steel tube filled with dry silica gel. The halomethanes were then condensed into a high pressure reservoir cooled with liquid nitrogen and separated from oxygen and nitrogen by at least five freeze-pump-thaw-cycles to a final pressure of 10^{-2} to 10^{-4} Pa.

For details of the apparatus cf. [6]. The self diffusion coefficients were determined by the pulsed field gradient method introduced by Stejskal and Tanner [7] in a Bruker MSL 300 spectrometer operating at a ^{19}F-resonance frequency of 282 MHz. The design of the home built probe head is given in [8].

In the presence of a pulsed field gradient, the decay of the echo amplitude A in a Hahn-spin-echo experiment is described by [7]

$$A(2\tau) = A(0)\exp\left(-\frac{2\tau}{T_2}\right)\exp(-\gamma^2 D\delta^2 \Delta - \tfrac{1}{3}\delta g^2). \tag{1}$$

In (1) τ is the time between the 90° and 180° pulse, γ the gyromagnetic ratio of the nucleus studied, D the self diffusion coefficient, δ the duration of the gradient pulses, Δ the time between the two gradient pulses, and g the gradient strength, given by $g = k\,I$. Here k means the coil constant, that has to be obtained from a calibration with a substance of known diffusion coefficient, and I the coil current.

The determination of D was most conveniently accomplished by increasing g while keeping all other variables constant. The coil constant was determined using the known self diffusion coefficient of water at ambient pressure and 298 K obtained by Mills [9], which is generally acknowledged to be the most reliable value [10]. The coil constant was controlled by a redetermination of D for benzene under standard conditions [11].

The self diffusion coefficients are judged reliable to ± 3%. Their reproducibility was depending on the temperature range ±1 to 2%.

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Results and Discussion

Tables 1 and 2 contain the D values determined for the two substances. In Figs. 1 and 2 some isobars of D are given. For CF_3Br and CF_3Cl saturation vapor pressure (SVP) data were available [12]: they are included in the Figures. Where for CF_3Br these data overlap with the results given here, they agree to $\pm 2\%$. For CF_3Cl the published SVP data show a smaller temperature dependence than our data. For $270\ \mathrm{K} > T > 195\ \mathrm{K}$ the deviation of the two data sets is within our experimental error, while at the highest temperatures the russian data are low. Around 140 K our data are about 10% below the published SVP-curve.

Activation Energies

Except for the saturation vapor pressure curves of D for $T > 250$ K and the high temperature end of the isobars for $p \leq 150$ MPa, the Arrhenius plots of Figs. 1 and 2 yield straight lines. The exception is caused by the large density changes at those high temperatures. From the linear sections of the isobars the activation energies at constant pressure ΔE_p^+, defined by

$$\Delta E^+ = -R\left(\frac{\mathrm{d}\ln D}{\mathrm{d}(1/T)}\right), \qquad (2)$$

is derived. Figure 3 gives the isochors for CF_3Br. From this diagram and the corresponding one for CF_3Cl (not shown) the activation energies at constant volume ΔE_ϱ^+ are deduced. The data are compiled in Table 3 and compared to those of other halomethanes. The densities for CF_3Br (14, 15) and CF_3Cl (16) were compiled from the literature and extrapolated by graphical procedures. It is typical for simple liquids to find the ratio $(\Delta E^+)_v/(\Delta E^*)_p \approx 0.5$ [17, 18]. This is fulfilled for all substances compiled in Table 3. The activation energies derived for the various substances behave rather unsystematic. Neither the size of the gas phase dipole moments (CF_4: 0 Debye, CF_3Cl: 0.5 Debye, CF_3Br: 0.65 Debye, CF_3H: 1.65 Debye, CH_3F: 1.85 Debye), nor the sequence adopted in Table 3, where the compounds are ordered with the molecular mass increasing from top to bottom, reveal any systematic trend. It is generally accepted that activation energies and activation volumes derived for the p, T-dependence of self diffusion or viscosity cannot be assigned to a physical process but may only be used for a qualitative intercomparison between different substances.

Table 1. Self diffusion coefficients $D(10^{-8}\ \mathrm{m^2/s})$ in CF_3Cl.

T[K]	SVP	p[MPa]				
		25	50	100	150	200
133	0.052	0.039	0.032	0.024	0.020	0.014
158	0.132	0.092	0.075	0.055	0.045	0.035
180	0.185	0.162	0.130	0.097	0.076	0.059
205	0.318	0.270	0.210	0.155	0.126	0.096
222	0.410	0.345	0.278	0.205	0.161	0.125
242	0.550	0.471	0.365	0.265	0.205	0.165
256	0.700	0.570	0.430	0.310	0.240	0.197
270	0.901	0.658	0.500	0.360	0.281	0.222
294	1.60	0.840	0.625	0.446	0.343	0.275
332		1.18	0.856	0.609	0.465	0.371
379		1.77	1.23	0.838	0.600	0.485
433		2.84	1.70	1.10	0.760	0.610

Table 2. Self diffusion coefficients $D(10^{-8}\ \mathrm{m^2/s})$ in CF_3Br.

T[K]	SVP	p[MPa]				
		25	50	100	150	200
141	0.043	0.032	0.027	0.019	0.013	0.0088
152	0.059	0.045	0.037	0.027	0.019	0.015
165	0.080	0.063	0.063	0.054	0.039	0.029
179	0.101	0.088	0.075	0.056	0.041	0.031
195	0.145	0.122	0.102	0.078	0.058	0.046
220	0.215	0.185	0.155	0.110	0.089	0.069
244	0.310	0.260	0.220	0.160	0.127	0.101
268	0.430	0.353	0.283	0.204	0.160	0.140
293	0.640	0.469	0.383	0.275	0.217	0.182
332		0.682	0.520	0.368	0.294	0.260
383		0.980	0.247	0.543	0.436	0.363
432		1.59	1.08	0.733	0.600	0.533

The data given in Table 3 seem to show that even for a sequence of very similar substances this does not lead to any deeper understanding of the influence of the single molecular properties upon self diffusion.

Hard Sphere Treatments

The interacting sphere model [5] ascribes the reduction of diffusivity in real liquids compared to the hard sphere molecular dynamics results to the attractive interaction approximated by a single Lennard-Jones potential,

$$D_{\mathrm{ex.}}^{(T,\,n)} = D_{\mathrm{LJ}} \equiv D_{\mathrm{HS}}(T, n, \sigma_{\mathrm{B}}) \exp(-\varepsilon/2\,kT). \qquad (3)$$

$n = \varrho\, \sigma_{\mathrm{B}}^3$ with ϱ the number density and σ_{B} the Boltzmann diameter. $D_{\mathrm{HS}}(T, n)$ is a fit equation for the molecular dynamics hard sphere self diffusion coeffi-

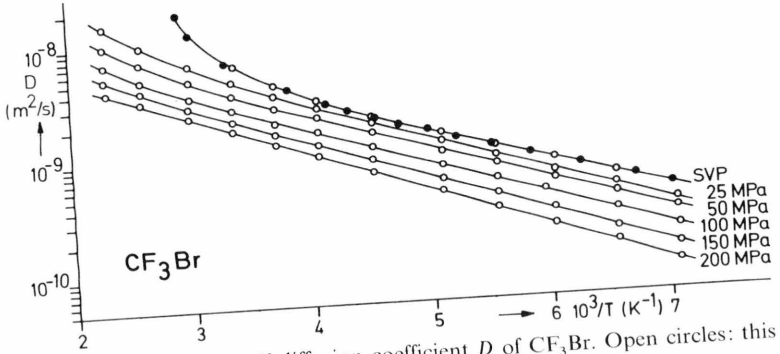

Fig. 1. Isobars of the self diffusion coefficient D of CF_3Br. Open circles: this work. Full circles: Ref. [12].

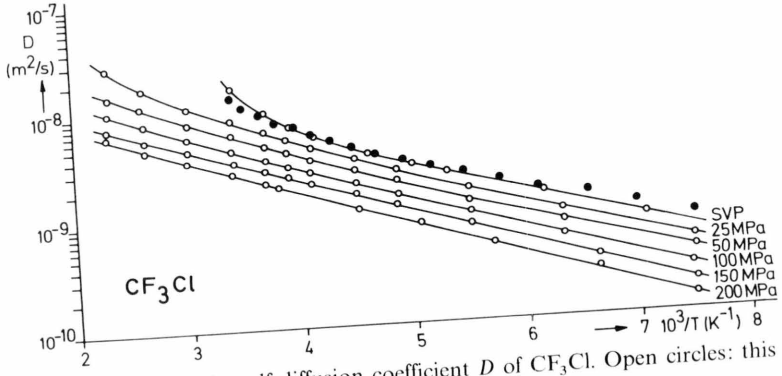

Fig. 2. Isobars of the self diffusion coefficient D of CF_3Cl. Open circles: this work. Full circles: Ref. [12].

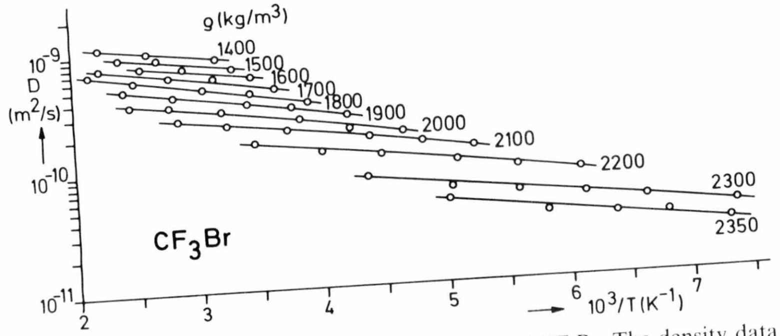

Fig. 3. Isochors of the self diffusion coefficient D of CF_3Br. The density data were partly obtained by extrapolation of literature values [14, 15].

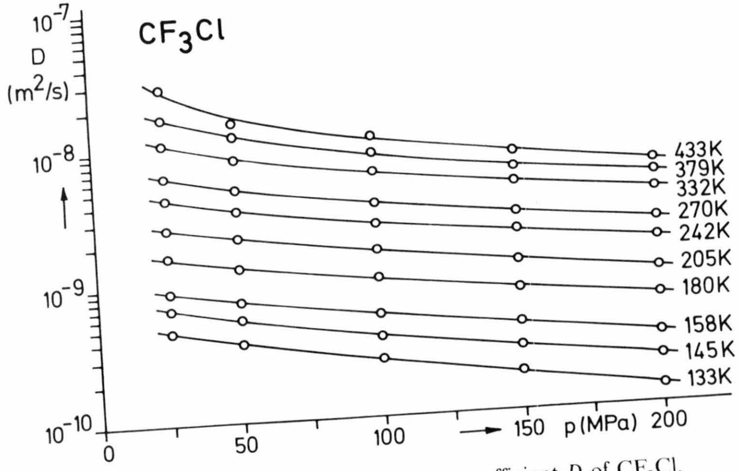

Fig. 4. Some isotherms of the self diffusion coefficient D of CF_3Cl.

cients obtained from a recent reassessment of published data [19].

$$D_{HS}(T, n) = (D_0/n)(1 - n/1.09) \cdot (1 + n^2(0.4 - 0.83\, n^2)), \tag{4}$$

$$D_0 = (3/8)\, \sigma_B (k_B\, T/\pi m)^{1/2}, \tag{5}$$

$$\sigma_B = \sigma_{LJ}(2/[1 + \sqrt{(2 k_B\, T/\varepsilon)}]^{1/6} \tag{6}$$

with k_B the Boltzmann constant, m the molecular mass and σ_{LJ} the Lennard Jones diameter.

This formalism describes all halomethanes studied hitherto with two parameters ε and σ_B that do predict a defined ϱ, T dependence for D. However, for the time being this analysis must rely on rather poor density data often obtained by long and crude extrapolations. In the high density region of the hard sphere fluid variation of $\pm 2\%$ in the density will change the self diffusion coefficient by $\sim 20\%$, the fairly large standard deviations observed in Table 4 results in our opinion mostly from systematic errors in our density extrapolation procedures. Evidently the description of all molecules without spherical symmetry by one radially symmetric Lennard-Jones potential is an approximation which describes an averaging over the different parts of the molecular surface.

Table 3. Activation energies at constant pressure and constant volume for a series of halomethanes.

Substance	Reference	$(\Delta E^+)_p$ [kJ/mol]	$(\Delta E^+)_V$ [kJ/mol]
CH_3F	(13)	5.0 ± 0.2	3.4 ± 0.1
CHF_3	(13)	6.1 ± 0.1	3.0 ± 0.3
CF_4	(6)	5.3 ± 0.2	2.6 ± 0.6
CF_3Cl		6.0 ± 0.2	2.7 ± 0.4
CF_3Br		6.6 ± 0.2	2.3 ± 0.4

Figure 5 compiles the results obtained from a fit of the CF_3Br self diffusion coefficients to Equation (2). In Table 4 the ε and σ_B values obtained for the various methane derivatives are given. The last three lines contain data for σ_B and ε taken from the literature they were derived from virial expansions of vapour pressure data [26] and low pressure viscosities [27, 28].

Conclusions

The self diffusion coefficients for all halomethanes studied hitherto and for methane can be well represented by the interacting sphere model. It will be very interesting to see whether systematic deviations from this concept occur, if more precise p, V, T-data become available for the whole region covered by these data, and if the data can still be represented by this approach when the self diffusion and density measurements are extended to pressures in the GPa-range.

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Table 4. Fit of diffusion data to (1).

Substance	Ref.	T/K	$\varrho\, \sigma^3$	σ_{LJ}/nm	(ε/k_B)/K	% Std. dev.
CH_4	(20)	110–328	0.33–0.89	0.414*	30*	2.3
				0.412	29	4.0
CF_4	(6)	140–432	0.2 –0.98	0.440*	244*	6.3
				0.452	88	6.8
CH_3Cl	(21)	210–440	0.53–0.88	0.436	129	8.2
CH_2Cl_2	(21)	186–406	0.65–1.02	0.479	162	3.3
$CHCl_3$	(21)	233–397	0.73–0.98	0.534	107	4.5
CCl_4	(22)	283–328	0.87–0.99	0.575	145	6.3
CH_3F	(23)	153–440	0.21–0.90	0.405	56	8.5
CHF_3	(24)	142–433	0.31–0.99	0.434	86	6.6
$CHClF_2$	(25)	147–383	0.49–1.04	0.461	164	6.8
CF_3Cl		133–433	0.45–0.99	0.473	181	8.0
CF_3Br		141–432	0.44–0.99	0.492	191	5.9
	(26)			0.530	195	
	(27)			0.492	222	
	(28)			0.486	220	

* For CH_4 and CF_4 the first entry was obtained from a fit to (3) by omission of the exponential term.

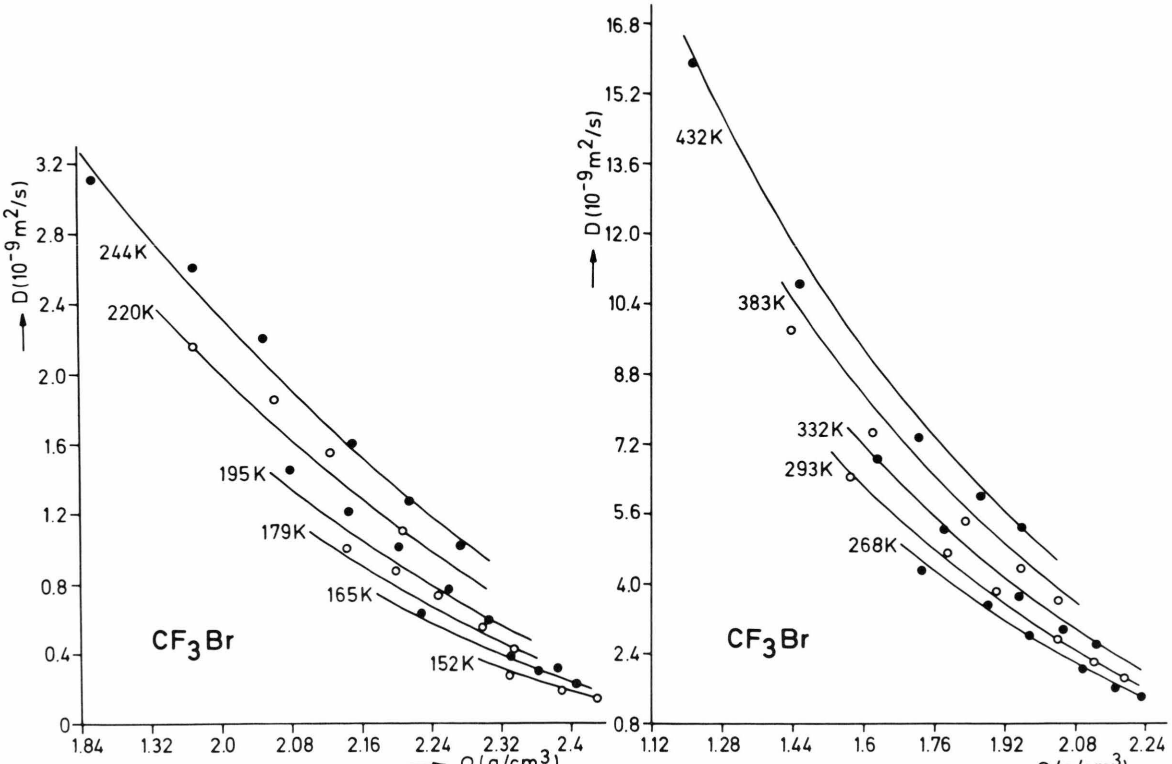

Fig. 5. Isotherms of the self diffusion coefficient of CF_3Br as function of particle number density $n = \varrho\, \sigma_B^3$. The lines drawn through the experimental points were obtained from a fit to (4). Fit parameters are given in Table 4.

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