

# Pressure Dependence of the Melting and Self Diffusion in 2,2-dimethylpropane, 2,2-dimethylpropionitrile, and 2-methylpropanol-2

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The melting pressure curves of 2,2-dimethylpropane, 2,2-dimethylpropionitrile and 2-methylpropanol-2 and the pressure dependence of the hex  $\rightleftharpoons$  fcc transition of 2,2-dimethylpropane have been determined in the pressure range between 0.1 and 200 MPa. The self diffusion coefficients  $D$  in the liquid state of the three compounds have been determined as function of pressure ( $p_{\max} \cong 120$  MPa) from the melting pressure curve up to ca. 450 K. At high temperatures and high pressures the self diffusion coefficients of the three compounds become rather similar. The influence of the hydroxylgroup upon the diffusivity of  $(\text{CH}_3)_3\text{COD}$  is most clearly seen at the lowest temperatures. The isobars of  $\text{C}(\text{CH}_3)_4$  and  $(\text{CH}_3)_3\text{CCN}$  are straight lines with identical slopes. For  $(\text{CH}_3)_3\text{COD}$  all isobars show a curvature. From the data in the Arrhenius representation activation volumes and activation energies are derived. For  $\text{C}(\text{CH}_3)_4$  the density dependence of  $D$  can be described with the rough hard sphere model.

## Introduction

The three title compounds were chosen for the study of the pressure dependence of the self diffusion coefficient because of their conformational rigidity and their approximately spherical shape. The comparison of the data obtained in a wide temperature and pressure range for 2,2-dimethylpropane and 2,2-dimethylpropionitrile ( $\mu = 3.95$  Debye) should yield information about the influence of a fairly large dipole moment upon the translational single particle diffusivity. The inclusion of 2-methylpropanol-2 ( $\mu = 1.70$  Debye) into the study should reveal the influence of hydrogen bonds upon the self diffusion. The self diffusion coefficients of the compounds chosen should provide an interesting test for theoretical models proposed for the dynamics of simple liquids. However, a thorough analysis of the data is possible only, if P,V,T-data are available for the P,T-range studied or can be extrapolated from existing data with reasonable accuracy. An extensive search through the literature yielded only for 2,2-dimethylpropane P,V,T-data [2, 3] suitable for extrapolation to the highest pressures studied: Since the apparatus used for the determination of

the self diffusion coefficients [1] at elevated pressures does only function properly if the complete pressurized sample is kept in the liquid or fluid state it was prerequisite to determine the melting pressure curves of the three compounds studied.

## Materials and Methods

2,2-dimethylpropane (purum) and 2,2-dimethylpropionitrile (purum) were obtained from Fluka AG (Buchs, Switzerland) and 2-methylpropanol-2 (p.a.) was purchased from E. Merck (Darmstadt, FRG). In order to simplify the proton spectrum, the hydroxylproton of 2-methylpropanol-2 was replaced by a deuteron by standard exchange procedures. All substances were further purified by distillation. The nitrile and the alcohol were stored over molecular sieve 3 Å.

## Instrumental

The self diffusion coefficients were obtained by the Hahn spin-echo-method [4] in a steady field gradient. The measurements were performed with the protons of the various molecules at 100.1 MHz on a modified Varian XL-100-15 FT NMR spectrometer. The details of the high pressure NMR cell [5] and the filling procedure of the cell have been published [6]. Also the design of the quadrupolar gradient coil and the calibration procedure have been described elsewhere [1].

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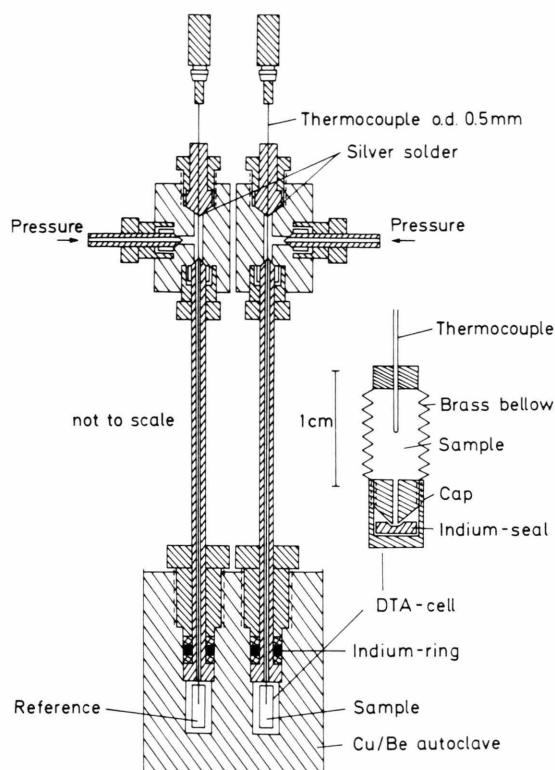


Fig. 1. High pressure apparatus for differential thermoanalysis. The diagram of the complete assembly is not to scale. (The autoclave proper has an o.d. of 80 mm and a height of 70 mm.)

### High-Pressure DTA-cell

Figure 1 gives a diagram of the high pressure DTA-cell used for the determination of the phase diagrams of the three substances. The autoclave is machined from a copper beryllium alloy (Berylco 25, Deutsche Beryllium, Oberursel, FRG). The two identical cells are connected to the same commercial high pressure system. Autoclave and pressure system are filled with a 1:1 mixture of methylcyclohexane and methylcyclopentane. The pressure is monitored by a 400 MPa Bourdon Gauge (Heise, Conn, U.S.A.) to  $\pm 0.5$  MPa. The two miniature metal sheathed chromel/alumel thermocouples (Philips, Kassel, FRG) are silversoldered into the bore of stainless steel nipples. The temperature of the sample, the temperature difference between sample and reference, and the pressure are monitored continuously on a three pen recorder. Heating and cooling is accomplished by putting the autoclave

into a liquid containing approximately 10 l of a precooled or preheated liquid. Heating rates between  $2 \text{ K} \cdot \text{min}^{-1}$  and  $25 \text{ K} \cdot \text{min}^{-1}$  can be obtained by this procedure. Sample and reference are contained in two brass bellows (Gebr. Witzemann, Pforzheim) described in the insert of Fig. 1. The miniature thermocouple is soft soldered into the top seal of the bellow. After filling the bellow with a syringe, the lower end is sealed off by pressing an indium plug with a cap onto the conical end of the seal.

In order to obtain a stable temperature difference between sample and reference outside the temperature range where phase transitions occur, one has to use a reference material that approximately matches the heat capacity of the sample. With this setup the phase transition temperatures can be measured in the temperature range between ca. 150 and ca. 400 K with an accuracy of  $\pm 0.5$  K.

### Results

In Fig. 2 the melting temperatures of the three title compounds and one solid-solid transition in 2,2-dimethylpropane are given. The experimental

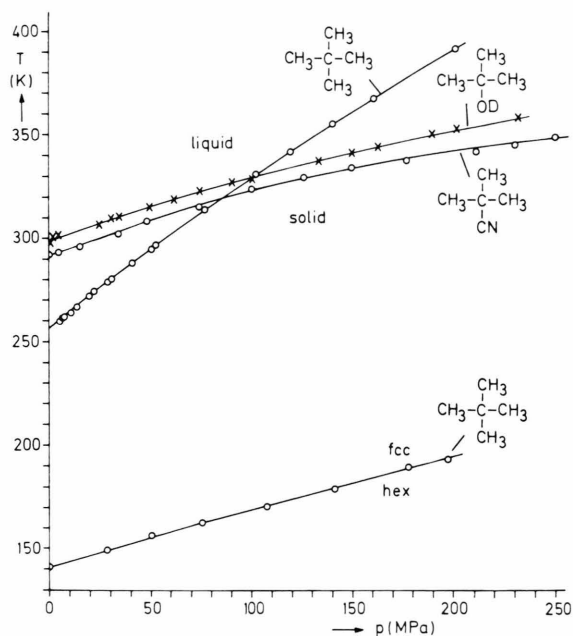


Fig. 2. Melting pressure curves of  $\text{C}(\text{CH}_3)_4$ ,  $(\text{CH}_3)_3\text{COD}$ , and  $(\text{CH}_3)_3\text{CCN}$ , and fcc  $\rightleftharpoons$  hex transition curve of  $\text{C}(\text{CH}_3)_4$ , determined by DTA.

Table 1. Description of the melting pressure curves of 2,2-dimethylpropane, 2,2-dimethylpropionitrile, and 2-methylpropanol-2 and of the pressure dependence of the hex  $\rightleftharpoons$  fcc transition in 2,2-dimethylpropane by polynomials of the form:  $T_{tr}(p) = T_0 + Ap + Bp^2$ .

| Compound                            | Phase trans.                 | Pressure range (MPa) | $T_0$ (K) | $A$ (MPa $^{-1} \cdot$ K) | $B$ (10 $^{-4}$ MPa $^{-2} \cdot$ K) | RMSD <sup>a</sup> (K) |
|-------------------------------------|------------------------------|----------------------|-----------|---------------------------|--------------------------------------|-----------------------|
| C(CH <sub>3</sub> ) <sub>4</sub>    | melting                      | 0.1 – 200            | 256.7     | 0.7759                    | – 5.406                              | 0.7                   |
| (CH <sub>3</sub> ) <sub>3</sub> CCN | melting                      | 0.1 – 250            | 292.2     | 0.3641                    | – 5.648                              | 0.8                   |
| (CH <sub>3</sub> ) <sub>3</sub> COD | melting                      | 0.1 – 225            | 298.7     | 0.3465                    | – 4.006                              | 0.7                   |
| C(CH <sub>3</sub> ) <sub>4</sub>    | hex $\rightleftharpoons$ fcc | 0.1 – 200            | 140.6     | 0.2992                    | – 1.718                              | 0.7                   |

<sup>a</sup> RMSD = Root mean square deviation.

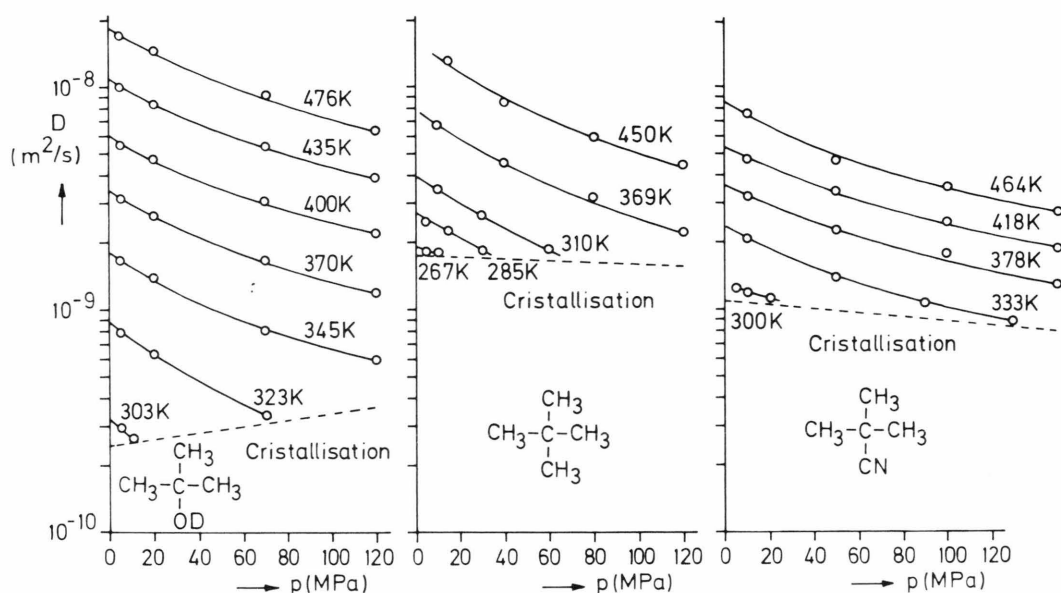


Fig. 3. Isotherms of the self diffusion coefficient  $D$  of C(CH<sub>3</sub>)<sub>4</sub>, (CH<sub>3</sub>)<sub>3</sub>COD, and (CH<sub>3</sub>)<sub>3</sub>CCN.

data for the four curves are within experimental accuracy described by simple polynomials of the form:

$$T_{tr}(p) = T_0 + Ap + Bp^2.$$

The parameters for the three substances are collected in Table 1. The data for the melting of 2-methylpropanol-2 agree with results given in the literature [7]. No data for the pressure dependence of the melting of 2,2-dimethylpropionitrile and 2,2-dimethylpropane were found in the literature, and also the pressure dependence of the solid-solid transition between the brittle hexagonal low temperature phase of 2,2-dimethylpropane and the plastic face centred cubic phase [8] appears to be unknown.

The increase of the melting temperature of 2,2-dimethylpropane with pressure (initial slope 0.78 K · MPa $^{-1}$ ) is unusually steep.

In order to assure proper pressure transmission into the NMR-cell one has to avoid partial crystallisation of the sample in the narrow neck of the glass cell, the self diffusion measurements were therefore limited to  $p \leq 120$  MPa for 2,2-dimethylpropane and 2-methylpropanol-2 and to  $p \leq 150$  MPa for 2,2-dimethylpropionitrile.

The isotherms of the self diffusion coefficients for the three compounds are presented in Figure 3. Figure 4 collects some isobars constructed from these data. The data were reproducible to better than  $\pm 5\%$ ; they are judged reliable to  $\pm 10\%$ .

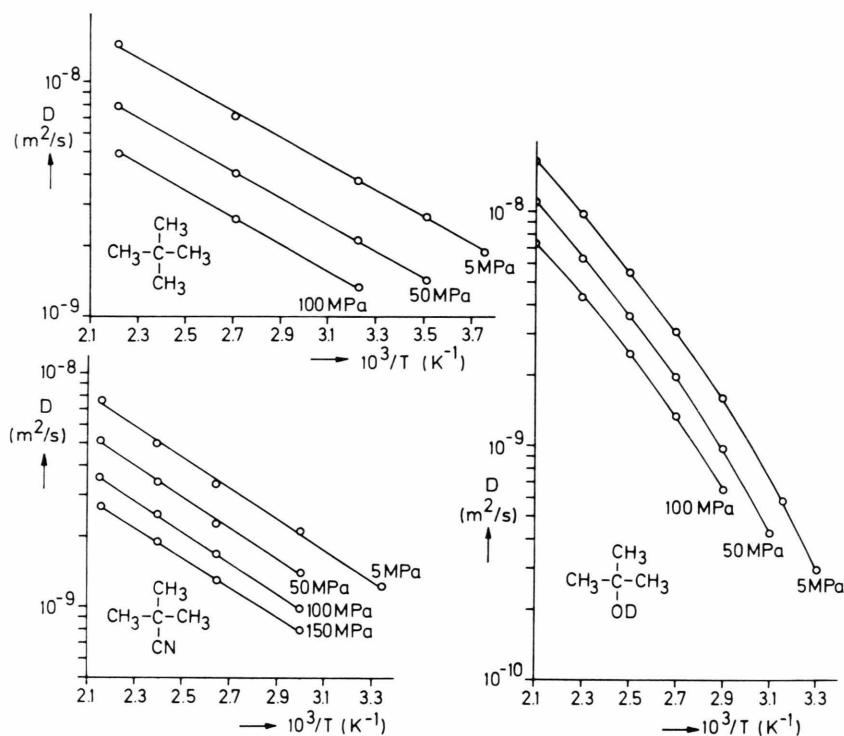


Fig. 4. Isobars of the self diffusion coefficient  $D$  of  $C(CH_3)_4$ ,  $(CH_3)_3COD$ , and  $(CH_3)_3CCN$ .

## Discussion

All isotherms of the three compounds show a pronounced curvature. The differences between the compounds are most clearly seen at temperatures below ca. 350 K. There the hydrogen bonded liquid 2-methylpropanol-2 shows by far the lowest molecular diffusivity. At temperatures above 450 K on the other hand, 2,2-dimethylpropionitrile possesses the lowest self diffusion coefficient.

The liquids investigated do have fairly different particle number densities at ambient temperature and pressure (2,2-dimethylpropane (20 °C):  $5.12 \cdot 10^{21} \text{ cm}^{-3}$ , 2,2-dimethylpropionitrile (25 °C):  $5.50 \cdot 10^{21} \text{ cm}^{-3}$  and 2-methylpropanol-2 (26 °C):  $6.09 \cdot 10^{21} \text{ cm}^{-3}$ ). It is to be expected that the three liquids will have quite different compressibilities and it appears thus indicated to compare the three liquids at the highest pressures, since here density differences would be smallest. From the slope of the isotherms the activation volume  $\Delta V_D^\ddagger$  for self diffusion can be calculated.

$$\Delta V_D^\ddagger = -RT \left( \frac{\partial \ln D}{\partial p} \right)_T. \quad (1)$$

$\Delta V_D^\ddagger$  is normally taken as a qualitative measure for the amount of additional space required by the molecule in the process of translational motion.

Table 2 collects the data at 100 MPa, the highest pressure at which the slope of the isotherms can be obtained with reasonable accuracy. For all compounds,  $\Delta V_D^\ddagger$  appears to decrease with falling temperature, though the effect is within the limits of experimental error for 2,2-dimethylpropane. The molecular volume for all compounds is around  $110 \text{ cm}^3 \text{ mol}^{-1}$ . The activation volumes for all three liquids amounts to 20–30% of this volume only. For the plastic crystalline phase of 2,2-dimethylpropane Allen *et al.* [9] determined an activation volume of  $110 \pm 20 \text{ cm}^3 \text{ mol}^{-1}$ . From the comparison of these data one may conclude that translational diffusion in the plastic crystal occurs in diffusional jumps between neighbouring lattice sites, while the translation of the molecules in the liquid state is a cooperative process involving smaller amplitude motions.

The decrease of  $\Delta V_D^\ddagger$  with falling temperature is in normal liquids observed for all transport properties, it seems to be a consequence of the changing

Table 2. Activation volumes  $\Delta V_D^\ddagger$  ( $10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ ) for self diffusion in liquid  $\text{C}(\text{CH}_3)_4$ ,  $(\text{CH}_3)_3\text{CCN}$ , and  $(\text{CH}_3)_3\text{COD}$  at 100 MPa. (All isotherms show a slight curvature, the slope of the isotherms has been determined at the highest common pressure possible.)

| Compound                    |                       |              |              |              |              |            |
|-----------------------------|-----------------------|--------------|--------------|--------------|--------------|------------|
| $\text{C}(\text{CH}_3)_4$   | Temperature (K)       | 369          | 450          |              |              |            |
|                             | $\Delta V_D^\ddagger$ | $27.5 \pm 3$ | $28.2 \pm 3$ |              |              |            |
| $(\text{CH}_3)_3\text{CCN}$ | Temperature (K)       | 378          | 418          | 464          |              |            |
|                             | $\Delta V_D^\ddagger$ | $17.0 \pm 3$ | $20.3 \pm 3$ | $21.9 \pm 3$ |              |            |
| $(\text{CH}_3)_3\text{COD}$ | Temperature (K)       | 345          | 370          | 400          | 435          | 476        |
|                             | $\Delta V_D^\ddagger$ | $23.7 \pm 3$ | $25.7 \pm 3$ | $27.8 \pm 3$ | $30.6 \pm 3$ | $35 \pm 3$ |

Table 3. Activation energies for self diffusion in liquid  $\text{C}(\text{CH}_3)_4$ ,  $(\text{CH}_3)_3\text{CCN}$  and  $(\text{CH}_3)_3\text{COD}$ .

| Compound                    | $(E_D^\ddagger)_p$<br>( $\text{kJ} \cdot \text{mol}^{-1}$ ) | $(E_D^\ddagger)_v$<br>( $\text{kJ} \cdot \text{mol}^{-1}$ ) | Pressure<br>range<br>(MPa) | Temp.<br>range<br>(K) |
|-----------------------------|---|---|----------------------------|-----------------------|
| $\text{C}(\text{CH}_3)_4$   | $10.4 \pm 1$  | $4.4 \pm 0.5$   | 0.1 – 120                  | 260 – 450             |
| $(\text{CH}_3)_3\text{CCN}$ | $13.3 \pm 1$  | —   | 0.1 – 150                  | 295 – 450             |
| $(\text{CH}_3)_3\text{COD}$ | $32 \pm 3$  | —   | 5                          | 310                   |
|                             | $22 \pm 3$  | —   | 5                          | 440                   |

density. Differences in density and compressibility are in our opinion also responsible for the smaller  $\Delta V_D^\ddagger$  values found for the nitrile at the higher temperatures. The similarity of the activation volumes derived for the alkane and the alcohol appear to indicate that specific molecular interactions like hydrogen bonds or large dipoles do not influence the pressure dependence of the transport properties.

All isobars of  $D$  for 2,2-dimethylpropionitrile and 2,2-dimethylpropane are linear in the Arrhenius-representation of Figure 4. In the pressure range studied the slope appears to be identical for all isobars of one compound. The isobars derived for the alcohol show a pronounced curvature, which is typical for all hydrogen bonded liquids.

From the slope of the isobars the activation energy at constant pressure

$$(E_D^\ddagger)_p = -R \left( \frac{\partial \ln D}{\partial (1/T)} \right)_p \quad (2)$$

can be derived. The data are collected in Table 3.

The activation energies for 2,2-dimethylpropane and 2,2-dimethylpropionitrile are very similar, while the presence of hydrogen bonds raises the activation energy for self diffusion by 10 to 20  $\text{kJ} \cdot \text{mol}^{-1}$ . The activation energy  $(E_D^\ddagger)_p$  for self diffu-

sion in the plastic crystalline phase of 2,2-dimethylpropane was found to lie between 25 and 33  $\text{kJ} \cdot \text{mol}^{-1}$  [9–12]. Melting thus reduces this activation parameter by a factor of approx. 0.3.

As stated in the introduction, we did not succeed in finding  $p, V, T$  data for the alcohol and the nitrile. Only for 2,2-dimethylpropane it was possible to extrapolate data extending to 40 MPa and 700 K [2, 3] with sufficient accuracy to study the density dependence of the transport properties. In Fig. 5 isotherms of the self diffusion coefficient of the alkane are plotted as function of density. From an Arrhenius-plot of the isochors constructed from this diagram in the range  $600 \leq \rho \leq 640$  ( $\text{kg} \cdot \text{m}^{-3}$ ) the

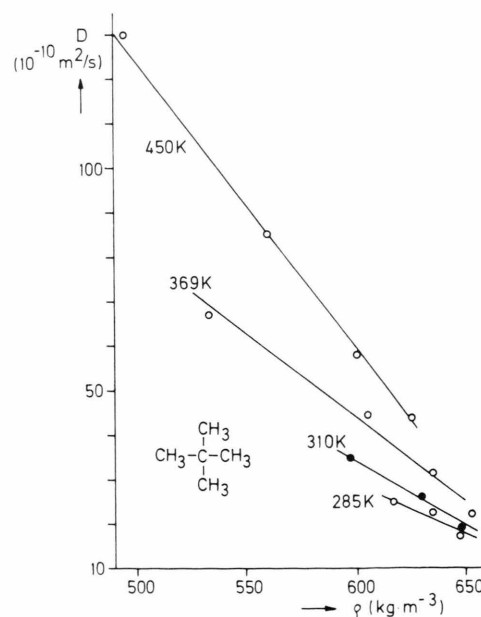


Fig. 5. Density dependence of the self diffusion coefficient  $D$  of  $\text{C}(\text{CH}_3)_4$ .



activation energy at constant density  $(E_D^\ddagger)_V = (4.4 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$  is derived. The ratio  $\frac{(E_D^\ddagger)_P}{(E_D^\ddagger)_V}$  is ca. 0.5 as commonly observed in simple non hydrogen bonded liquids [13].

It is now generally accepted that the concept of an activated transition state becomes dubious in condensed systems, especially if kinetic processes are concerned that are very rapid and yield activation energies similar to the thermal energy of the system. The activation data presented here should thus be taken as a convenient and compact description allowing a qualitative intercomparison between various liquids.

The density and temperature dependence of the self diffusion coefficient of liquids composed of conformationally rigid approximately spherical molecules can be described by the corrected Enskog theory [14] as applied by Dymond [15] in the smooth hard sphere model. The self diffusion coefficient of the smooth hard sphere liquid  $D_{\text{shs}}$  is presented in terms of the packing fraction  $\varrho d^3$  [15, 16]

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

where  $m$  is the molecular mass,  $d$  the hard sphere diameter and  $\varrho$  the number density.  $P(\varrho d^3)$  is an empirical polynomial of the packing fraction  $\varrho d^3$ . It is derived from a fit of the molecular dynamics results of a hard sphere fluid as obtained by Alder *et al.* [17]. For liquids composed of real molecules one has to expect deviations from the ideal spherical shape and to consider directional interactions caused for instance by dipole moments or hydrogen bonds. All these effects can lead to rotation-translation coupling and lower, compared to the case of the smooth hard sphere, the self diffusion coefficient. Chandler [16, 18, 19] has introduced the concept of the rough hard sphere liquid. The self diffusion coefficient of this liquid  $D_{\text{rhs}}$  is given by

$$D_{\text{exp}} \cong D_{\text{rhs}} = A D_{\text{shs}}, \quad (4)$$

where  $D_{\text{rhs}}$  and  $D_{\text{shs}}$  are the self diffusion coefficients of the rough and smooth hard sphere at the same packing fraction  $\varrho d^3$  and  $A$  characterizes the degree of rotation-translation coupling. Since the hard sphere diameter has to be derived from the experimental data, it is customary to use the measured isothermal density dependence of the self

| $T$ (K) | $d$ (nm) | $A$  |
|---------|----------|------|
| 400     | 0.55     | 0.81 |
| 369     | 0.54     | 0.54 |
| 310     | 0.55     | 0.55 |
| 285     | 0.55     | 0.44 |

Table 4.  
Hard sphere diameters  $d$  (nm)  
and  $A$  parameters  
( $A \equiv D_{\text{exp}} \cdot D_{\text{shs}}^{-1}$ ) of liquid  
2,2-dimethylpropane.

diffusion coefficient  $\left. \frac{\partial \ln D}{\partial \ln \varrho} \right|_T$  together with the density dependence of the smooth hard sphere fluid

$\left. \frac{\partial \ln D_{\text{shs}}}{\partial \ln (\varrho d^3)} \right|_T$  to obtain the hard sphere diameter [15, 16, 20]. From the data given in Fig. 5, the hard sphere diameter  $d$  and the parameter  $A$  are derived. They are collected in Table 4. While  $d$  appears to be independent of temperature,  $A$  decreases significantly with falling temperature. For an apolar symmetrical molecule this can only mean that the deviation of the molecule from perfect spherical symmetry becomes considerably more effective if the thermal energy is lowered. The same tendency was observed for the analysis of the self diffusion of liquid trifluoromethane [1]. In the first studies of the rough hard sphere model, where carbontetrachloride was analysed over a temperature range of ca. 50 K [16] a temperature independent hard sphere diameter of 0.525 and a constant  $A$  of 0.54 was found. Parkhurst and Jonas [21] studied  $D$  in tetramethylsilane and benzene as function of pressure and temperature and found that  $A$  and  $D$  are practically independent of temperature. In the case of tetramethylsilane however, which is the only compound strictly comparable to the tetrahedral molecules studied here, their data were collected between 298–373 K only, and thus end 120 K above the melting point of tetramethylsilane (151 K). Even in this limited range,  $A$  increases from 0.56 to 0.62. Though this change might be at the limit of the accuracy of the data analysis it parallels the effect observed in  $\text{CF}_3\text{H}$  and  $\text{C}(\text{CH}_3)_4$ .

It appears interesting to note that the hard sphere diameter  $d$  derived for  $\text{CCl}_4$ ,  $\text{C}(\text{CH}_3)_4$ , and  $\text{Si}(\text{CH}_3)_4$  corresponds within  $\pm 0.02 \text{ nm}$  to the smallest possible contact distance of the “tetrahedra” constructed with the known bondlengths and van der Waals radii, i.e. to two tetrahedra approaching each other face to face. The diameter  $d$  derived from the self diffusion coefficients is 0.53 nm in  $\text{CCl}_4$ , 0.55 nm in  $\text{C}(\text{CH}_3)_4$  and increases to 0.57 in

$\text{Si}(\text{CH}_3)_4$ . The diameter of the sphere incorporating the complete van der Waals cloud of the tetrahedra is 0.71 nm for  $\text{CCl}_4$  and  $\text{C}(\text{CH}_3)_4$ , and 0.77 nm for  $\text{Si}(\text{CH}_3)_4$ . In order to analyze whether the self diffusion coefficients in liquid  $(\text{CH}_3)_3\text{COD}$  and  $(\text{CH}_3)_3\text{CN}$  can also be described with the concept of the rough hard sphere fluid, one would need reliable density data. Inspection of the isotherms of the three compounds given in Fig. 3 reveals that the pressure dependence is very similar for these substances, and one would predict that the most significant difference would be a stronger variation of the coupling parameter  $A$  with temperature. In the high temperature region  $T > 400$  K all three compounds appear to possess similar coupling parameters  $A$ . It is to be expected that in  $(\text{CH}_3)_3\text{COD}$  lowering of

the temperature leads to a pronounced enhancement of the translation-rotation coupling because of the increasing formation of hydrogen bonds. The parameter  $A$  of this compound should thus decrease much faster with falling temperature than observed for the unpolar tetrahedral compounds discussed above, and also the large dipole moment of  $(\text{CH}_3)_3\text{CCN}$  should in the low temperature range cause a higher degree of rotation-translation coupling.

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