

Pressure and Temperature Dependence of Self-Diffusion in Liquid Linear Hydrocarbons

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The pressure and temperature dependence of the self-diffusion coefficients D of n-butane, n-pentane, n-hexane, n-decane, trans-2-butene, cis-2-butene and 2-butyne were determined in the liquid state by NMR-techniques at pressure up to 200 MPa and temperatures up to 450 K.

The results are taken as tests for the various dynamical models and compared to results obtained by MD calculations. The activation parameters for translational transport and the parameters for the RHS-model are derived and discussed.

Introduction

During the last years several groups studied the temperature and pressure dependence of translational diffusion in simple rigid methane derivatives [1, 2, 3, 4]. The data obtained for these compounds have been used as tests for simple dynamical models like the activation theories, the free volume model [5] and the hard sphere model [6, 7]. In addition the self diffusion coefficients were compared to results obtained from MD simulations [8, 9, 10].

For the methane derivatives it can be shown that the rough hard sphere model gives the best description of the data, though it still remains impossible to extrapolate reliably with any of the existing models into regions of the p, T space not covered by the experiments.

In the present paper several nonpolar hydrocarbons are investigated in order to learn whether the conformational flexibility of these compounds introduces new complications in the application of the dynamical models and whether the shift of the trans \rightleftharpoons gauche equilibria which is predicted to occur with increasing density in direction to the more compact gauche forms [11, 12, 13], changes significantly the pressure dependence of the self diffusion coefficients.

The investigations started with this paper are aimed at characterizing the intra- and intermolecular dynamics of n-butane in a wide range of

densities and temperatures. In the work presented here the self diffusion coefficients of n-butane are compared to the corresponding quantities in n-pentane, n-hexane and n-decane in order to learn something about the influence of the size, the mass and the multiple trans \rightleftharpoons gauche equilibria upon the results.

2-butyne, 2-trans- and 2-cis-butene are included in this study as conformationally rigid molecules of varying shape but almost identical mass.

Experimental

The self-diffusion coefficients were measured in a strengthened glass cell apparatus [14] by the spin echo technique using a steady field gradient. They were measured at 100.1 MHz in a modified Varian XL-100-15 FT spectrometer. Details of the experimental setup and the filling procedures have been given previously [3, 15]. The field gradient was calibrated before the start of each series of experiments using the known self-diffusion coefficients of water [16]. The temperatures are accurate to ± 1.5 K. The self-diffusion coefficients obtained were reproduced to $\pm 3\%$. They are judged reliable to $\pm 10\%$.

Substances

Butane (99.5%), trans-2-butene (95%, 4% cis-2-butene), cis-2-butene (95%, 3.5% trans-2-butene)

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were purchased from E. Merck (D-6100 Darmstadt). 2-butyne (> 99%), pentane (99.8%) puriss., hexane (99.7%) puriss., decane (99.5%) puriss. were obtained from Fluka (Buchs, Switzerland). The gases were stored in 5 L flasks over molecular sieve 3 Å in order to absorb residual moisture.

Prior to use all compounds were degassed by several freeze-pump-thaw-cycles to a final pressure of 5 mPa.

Results and Discussion

Figures 1 to 3 collect the isotherms of the self-diffusion coefficients for all compounds measured. Figures 4 and 5 give in addition the data for butane, butyne and decane in the form of Arrhenius-plots. Most isotherms reveal in the $\log D$ versus p plot a curvature. Also in the Arrhenius-plots significant deviations from linearity are seen.

It is thus obvious that the description of the self-diffusion data with the concept of the transition state theory by means of the activation energies E_A and activation volumes ΔV^\ddagger does lead to activation parameters that depend on temperature and pressure. However, it is customary to derive such data for an intercomparison of various substances. For all compounds $(E_A)_p$ defined by

$$(E_A)_{p=\text{const}} := -R \left(\frac{\partial \ln D}{\partial 1/T} \right)_p \quad (1)$$

was calculated for the reduced temperature $T \cdot T_c^{-1} = 0.56$, where T_c is the critical temperature, and also the activation volumes ΔV^\ddagger , given by

$$\Delta V^\ddagger = -RT \left(\frac{\partial \ln D}{\partial p} \right)_T, \quad (2)$$

were evaluated at various temperatures for a pressure of 120 MPa. It appeared most meaningful to use this high pressure in order to minimize the influence of the changing density. The results for the activation energies at constant pressure are compiled in Figure 6. It is apparent that for all conformationally flexible compounds $(E_A)_p$ increase with rising pressure, the effect being most pronounced for n-decane. The sterically rigid substances show less pressure dependence. For trans-2-butene and 2-butyne $(\Delta E_A)_p$ appears to be constant in the region studied.

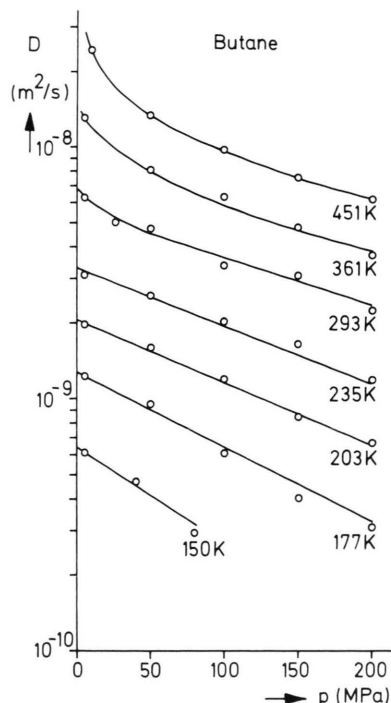


Fig. 1. Isotherms of the diffusion coefficients of fluid n-butane.

Only for n-butane [17–21], n-pentane [17, 18, 19, 22–26], n-hexane [17, 18, 19, 23, 27, 28] and n-decane [17, 18, 19, 29] there exist sufficient pVT data in the literature to calculate also the activation energies at constant density. The isochores of the self-diffusion coefficient constructed from these data show a slight curvature in the high temperature region. From the slope of the isochores at their low temperature end one obtains the activation energies compiled in Table 1. In n-butane and n-pentane the increase of $(E_A)_V$ with density is within the limits of experimental error in the region of our experiments. However in hexane and decane a significant increase with rising density is seen, and it is thus to be expected that more precise measurements or extension of the data to higher pressures would firmly establish a density dependence of $(E_A)_V$ for these compounds also.

Comparison of the activation energies derived at constant pressure and constant density shows that the ratio $[(E_A)_V][(E_A)_p]^{-1}$ is close to 0.5, a value typical for nonassociated liquids.

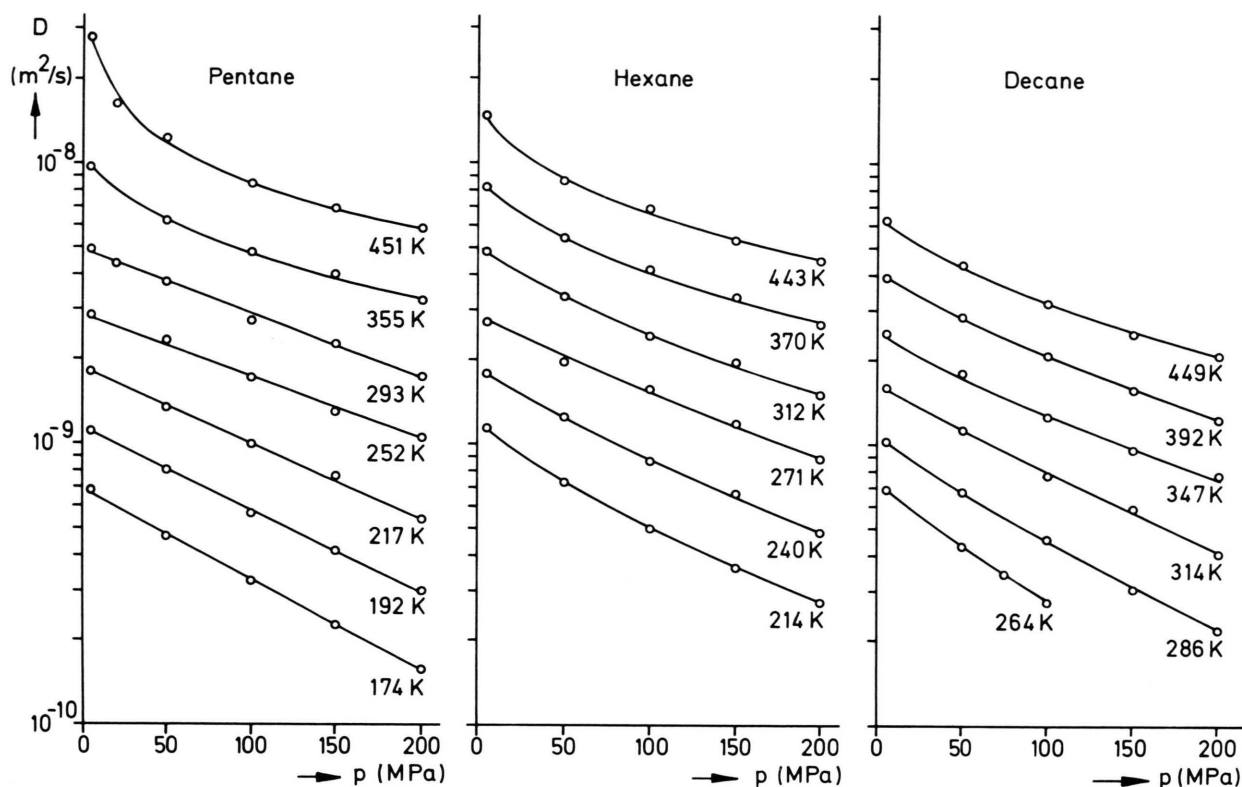


Fig. 2. Isotherms of the self diffusion coefficients of fluid n-pentane, n-hexane and n-decane.

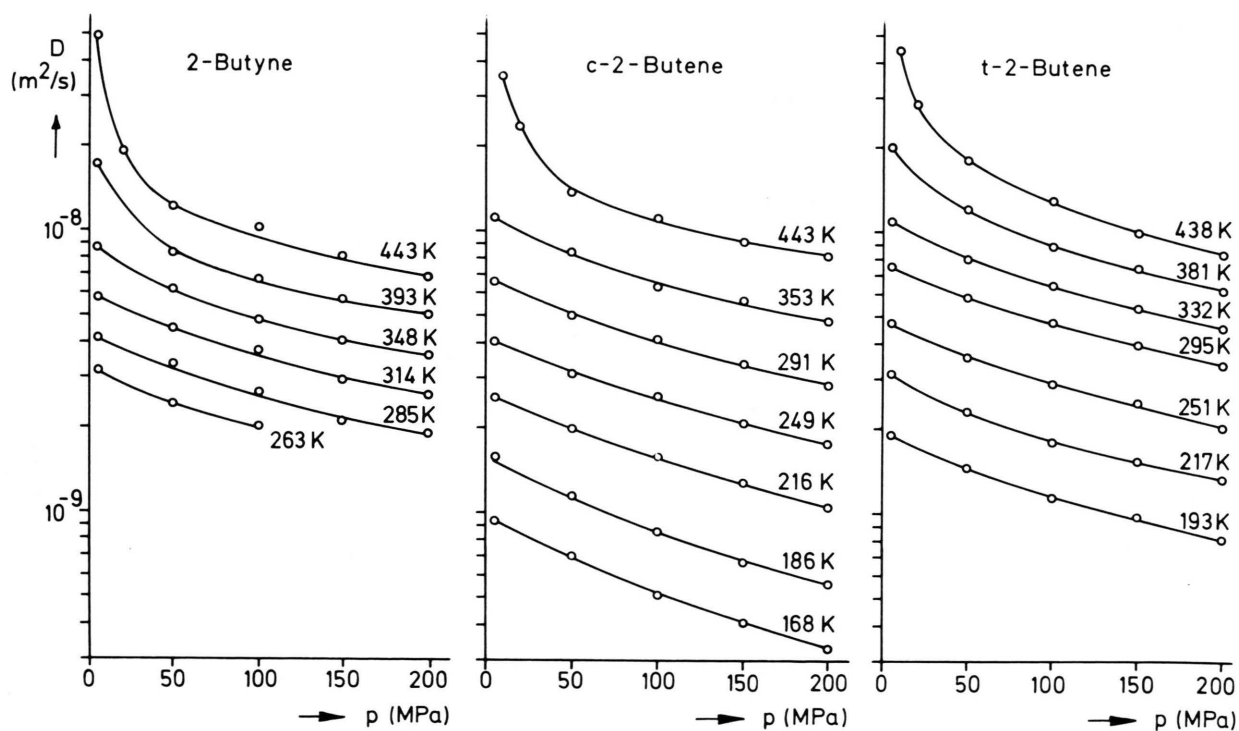


Fig. 3. Isotherms of the self diffusion coefficients of fluid 2-butyne, c-2-butene, and t-2-butene.

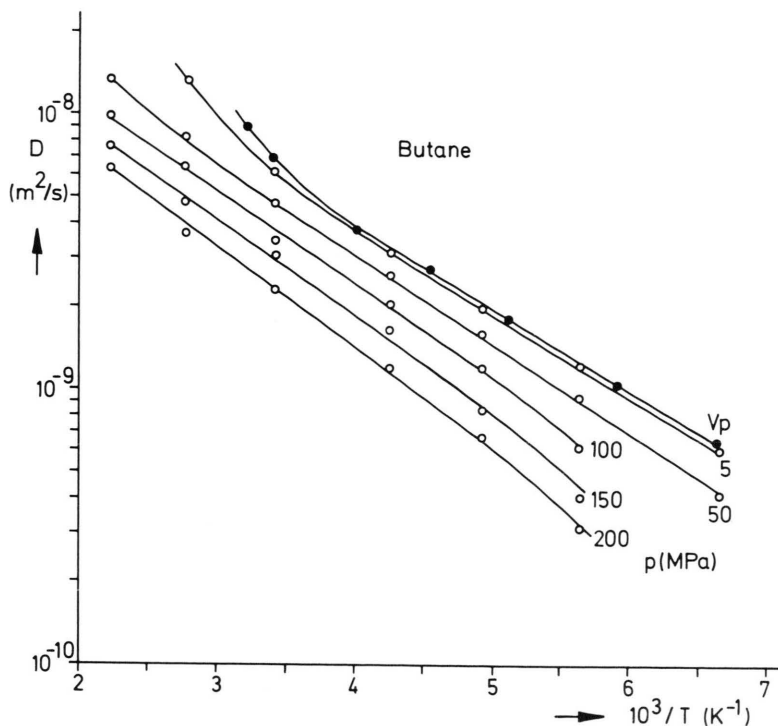


Fig. 4. Arrhenius diagram of the self diffusion coefficient of fluid n-butane.

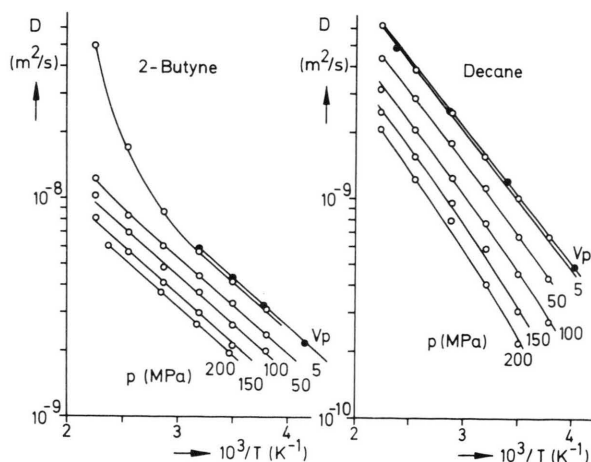


Fig. 5. Arrhenius diagrams of the self diffusion coefficients of fluid 2-butyne and n-decane.

Figure 7 gives the activation volumes at 120 MPa as function of temperature. ΔV^\ddagger increases for all compounds with rising temperature. All n-alkanes reveal a fairly uniform change with temperature. The activation volumes derived for 2-butyne coincide under the conditions chosen with the results of c-2-butene. These two compounds and t-2-butene do show a significant stronger tempera-

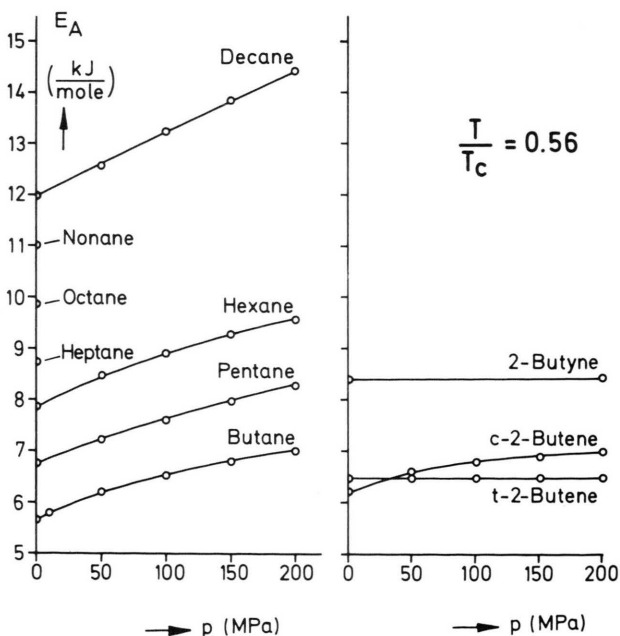


Fig. 6. Pressure dependence of the activation energies at constant pressure for D at a common reduced temperature $T/T_c = 0.56$. (T_c = critical temperature; $T_c(\text{C4}) = 425 \text{ K}$, $T_c(\text{C5}) = 470 \text{ K}$, $T_c(\text{C6}) = 507 \text{ K}$, $T_c(\text{C10}) = 618 \text{ K}$.)

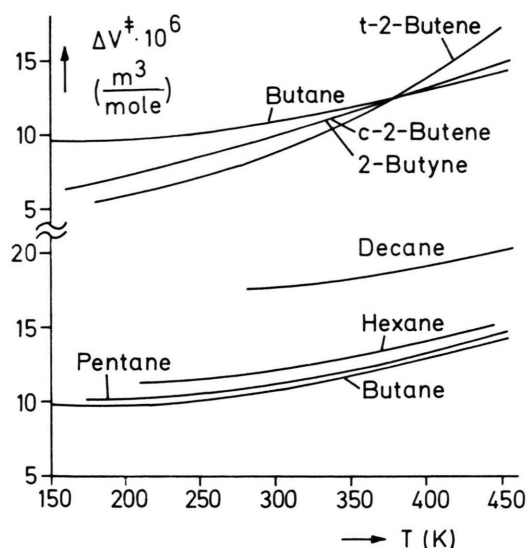


Fig. 7. Temperature dependence of the activation volumes for D at 120 MPa derived from the data in Figs. 1 to 3. The ΔV^\ddagger for 2-butyne coincide in the temperature range where it could be measured (285–450 K) with the ΔV^\ddagger for c-2-butene.

Table 1. Density dependence of the activation energies at constant volume (E_A) $_{V=\text{const}}$ (error $\pm 10\%$).

Substance	Density range ($\text{kg} \cdot \text{m}^{-3}$)	(E_A) $_{V=\text{const}}$ ($\text{kJ} \cdot \text{mol}^{-1}$)
Butane	600–735	2.7–3.1
Pentane	625–725	3.3–3.9
Hexane	650–750	3.2–4.3
Decane	700–800	5.5–7.7

ture dependence of ΔV^\ddagger than n-butane. It appears impossible to correlate ΔV^\ddagger or its temperature dependence quantitatively with any geometrical features of these simple molecules. The three activation parameters derived above show clearly, that their variation with temperature and pressure prohibits the use of these parameters as well as their p and T dependence for the extrapolation of transport data into regions not covered by experiment.

These activation data can only be used for a qualitative intercomparison of the transport processes in different substances. Among the simple models in use for the description of dynamic data

the rough hard sphere model (RHS-model) introduced by Dymond [6] and Chandler [7] proved most useful for the correlation of self-diffusion data. Compounds like the chloro- and fluoromethane derivatives CH_3Cl , CH_2Cl_2 , CHCl_3 , CF_3H , CH_3F [4], benzene [30], methanol [31] and even water [32] can be described quantitatively by this model.

In this model, results of the gas kinetic Chapman-Enskog theory [33, 34] are combined with the molecular dynamics simulations of the hard sphere model fluid [35].

The diffusion coefficient D_0 for a dilute gas composed of hard spheres is given by [33]

$$D_0 = \frac{3}{8n\sigma^2} \left(\frac{kT}{m\pi} \right)^{1/2} \quad (3)$$

with n the number density and σ the hard sphere diameter. For dense gases Enskog [34] scaled this expression with the radial distribution function $g(\sigma)$

$$D_E = D_0/g(\sigma). \quad (4)$$

Computer simulations on hard sphere model systems by Alder and his group [35] revealed the existence of correlations between the molecular velocities of nearest neighbour molecules. According to these results, D can be expressed after introduction of the self-diffusion coefficient for a smooth hard sphere D_{SHS} by

$$D = \frac{D_0}{g(\sigma)} \left(\frac{D_{\text{SHS}}}{D_E} \right). \quad (5)$$

The quotient (D_{SHS}/D_E) is derived from a fit to Alder's simulation data. Dymond [6] gives for D_{SHS} the equation

$$10^9 D_{\text{SHS}} = 2.527 \left(\frac{RT}{M} \right)^{1/2} V_0^{-2/3} (V - 1.384 V_0) \quad (6)$$

which is valid in the density range $1.5 \leq V/V_0 \leq 2$, with V_0 the molar volume of a hard sphere at close packing:

$$V_0 = N_A \frac{\sigma^3}{\sqrt{2}}.$$

There exist in the literature various empirical equations [7, 36] which lead in the density range of the experiments given here to identical results.

According to Chandler, translation-rotation coupling should lead to a lowering of the experimental

diffusion coefficients in real, polyatomic liquids. The experimental diffusion coefficient D_{exp} should thus correspond to the diffusion coefficient of a rough hard sphere D_{RHS} given by

$$D_{\text{exp}} \approx D_{\text{RHS}} = A_D D_{\text{SHS}} \quad (A_D \leq 1),$$

where A_D characterizes the extent of rotation-translation coupling. This leaves two free parameters for the description of self diffusion data as function of density and temperature: the diameter of the hard sphere d and the parameter A . Our previous experiments showed that the data obtained between the melting pressure curves of various substances at 450 K and at pressures up to 200 MPa can be fitted with a temperature independent RHS-diameter d_{RHS} and an A -parameter that increases with rising temperature.

For theoretical reasons one would expect that d_{RHS} should also reveal a slight decrease with temperature. Within the accuracy of our data for methane derivatives mentioned above and also for 2,2-dimethylpropane, 2,2-dimethylpropionitrile and 2-methylpropanol-2 [37] d_{RHS} is constant. The same is derived from the evaluation of the results for the

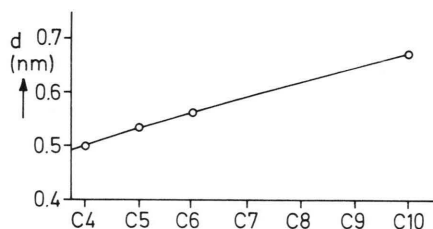


Fig. 8. Rough hard sphere diameter d for the n-alkanes C4, C5, C6 and C10 as derived from application of (6) to the experimental data.

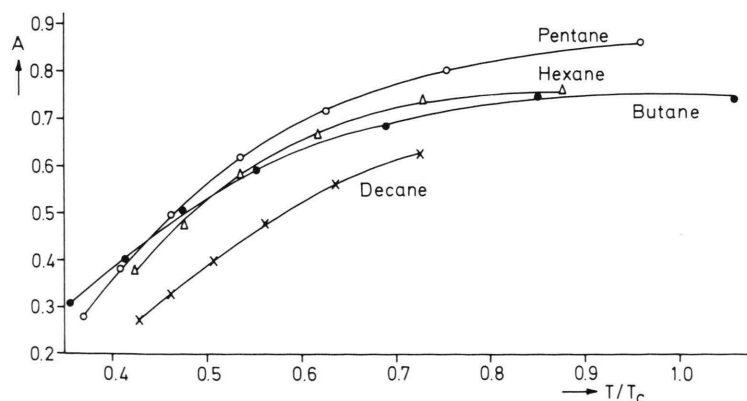


Fig. 9. Temperature dependence of the A -parameter of the RHS model characterizing the extent of rotation-translation coupling for the four n-alkanes.

Table 2. Comparison of the molar volumes V_0 calculated by application of the RHS model with the same quantity calculated from melting point densities.

Molar volume	Substance			
	Butane	Pentane	Hexane	Decane
$V_0 \left(\frac{\text{m}^3}{\text{mol}} \cdot 10^6 \right)$	52.6	64.2	75.7	129.0
$N_L \frac{d^3}{\sqrt{2}} \left(\frac{\text{m}^3}{\text{mol}} \cdot 10^6 \right)$	52.9	64.5	76.0	129.2

n-alkanes, though the concept of a hard sphere diameter for this flexible prolonged molecules is certainly questionable. Figure 8 gives the d_{RHS} derived. They increase monotonically from a value of 0.5 nm for n-butane to a value of 0.67 nm for n-decane. The molar volumes calculated from the RHS-diameter correspond quantitatively to the molar volumes of the solid compounds at the atmospheric pressure melting temperature, an observation that has been made for other compounds also. The data are collected in Table 2. The only free quantity in the fitting procedure is thus the rotation translation coupling parameter A .

Figure 9 collects the A -parameters of the four n-alkanes. In general they increase from a value around 0.3 above the melting point to about 0.8 around the critical temperature. For the three lighter compounds no systematic variation of A with chain length is seen, within the limits of accuracy they seem to coincide. Compared to butane, pentane and hexane, the A -parameter of decane is significantly lower at the corresponding reduced temperature.

Table 3. Comparison of the self diffusion coefficients obtained experimentally and by MD simulations.

	<i>T</i> (K)	<i>P</i> (MPa)	$D \left(\frac{\text{m}^2}{\text{s}} \cdot 10^8 \right)$	
			<i>D</i> _{MD}	<i>D</i> _{exp}
n-Butane	397.83	4.2	4.91 *	2.5
	406.04	15.42	3.36 *	1.52
	314.86	8.97	1.74 *	0.76
	416.42	39.61	2.19 *	1.26
	407.27	101.96	1.50 *	0.78
	291.5	S.P.	6.1/6.9 **	6.7
	199.9	S.P.	2.1/2.4 **	1.97
n-Decane	481	S.P.	7.5/7.7 **	7.6

* Weber, Ref. [39]. – ** Ryckaert, Ref. [40, 41].

Inspection of the Figs. 8 and especially 9 reveals clearly that the interpolation of *D* for unknown homologues could only be achieved with some degree of reliability if a theoretical concept for the temperature dependence of the *A*-parameter would be available. The present state of the art makes extrapolations into unknown ranges of the *q*, *T*-space as well as interpolation of the data to cover unknown intermediate homologues equally hazardous.

Comparison with Computer Simulations

The most recent calculations concerning the properties of liquid hydrocarbons are the Monte Carlo

simulations by W. J. Jorgensen et al. [38]. The dynamic properties of butane as functions of pressure and temperature were calculated with molecular dynamics simulations by Weber [39] using a simplified skeleton alkane model and a simplified Lennard-Jones 6–9 interaction potential.

Ryckaert et al. [40, 41] used a similar approach applying a 6–12 Lennard-Jones potential to derive the thermodynamic and dynamic behaviour of liquid n-butane and n-decane close to their boiling points at atmospheric pressure. Table 3 compares their calculated self diffusion coefficients with our interpolated experimental results.

While the Ryckaert's results agree with our data within the limits of experimental error, Weber's treatment yields self diffusion coefficients that are approximately a factor of two larger than our results. Considering the similarity of the two computational approaches this large difference is surprising. However, one should check experimentally various other properties before any attempt is made to evaluate the merits and shortcomings of the two approaches.

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