

# MEASUREMENTS OF THERMAL DIFFUSIVITY IN PURE FLUIDS AND BINARY LIQUID-GAS MIXTURES BY DYNAMIC LIGHT SCATTERING

E. Reile and J. Straub  
Technische Universität München  
München, Federal Republic of Germany

## ABSTRACT

By means of measurements on CO<sub>2</sub> we show that dynamic light scattering supplies reliable thermal diffusivity data. Dynamic light scattering is then used to measure the decay rate of fluctuations along the saturation line and on the critical isochore for CO<sub>2</sub>, SF<sub>6</sub> and CHF<sub>3</sub> as well as for binary mixtures SF<sub>6</sub>-CO<sub>2</sub> and SF<sub>6</sub>-CHF<sub>3</sub>.

In addition, measurements of refractive index and concentration of saturated liquid and gas phase are presented.

## INTRODUCTION

Up to now dynamic light scattering [1,2] mainly was used to investigate the decay of density fluctuations in pure fluids near the critical point and the decay of concentration fluctuations in binary liquid-liquid mixtures near the consolute critical point. In the first case thermal diffusivity  $a = \Gamma/q^2$  can be determined from the decay rate  $\Gamma$  ( $q$  is the scattering vector), while in the second case we get mass diffusivity  $D = \Gamma/q^2$ .

We used these methods to measure order parameter dynamics in binary liquid-gas mixtures, where in principle fluctuations of density ( $\rho$ ) and concentration ( $x$ ) are both important. However, the contribution of concentration fluctuations to the scattered light was very small, as the components of our mixtures show only small variations in refractive index. We also could not see any deviation from a single exponential behaviour of the measured correlation functions. So we believe that what we could observe in our measurements was only the decay of density fluctuations, and the transport coefficient is thermal diffusivity.

For all of the pure fluids and mixtures investigated, we find that the data for the gas phase and the critical isochore are described by a single power law

$$a = a_0 |1 - T/T_c|^\beta \quad (1)$$

For our measurements of refractive indices and concentrations of the saturated liquid and gas phase, the density and concentration may be described by

$$\rho_l - \rho_g = \rho_c B(1 - T/T_c)^\beta \quad (2)$$

and

$$x_g - x_l = B'(1 - T/T_c)^{\beta'} \quad (3)$$

## EXPERIMENTAL METHOD

For our measurements we used a homodyne dynamic light scattering apparatus (Fig.1) as described in [1,2], e.g., with scattering angles of 3° to 20° and a long sample cell (110 mm) to reduce stray light from the high quality windows.

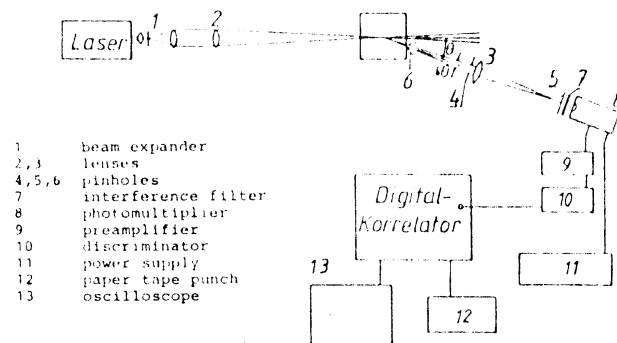


Fig. 1: Schematic of the light scattering apparatus

Measurements of refractive index are done by a simple refractometer according to Fig.2. The accuracy of  $n$  is about  $3 \cdot 10^{-4}$ .

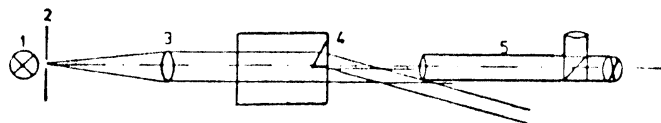


Fig. 2: Schematic of refractive index measurements

Concentration in the case of binary mixtures are measured by gas-chromatography after all light-scattering and refractive index measurements, so that these data are all taken at the same mean density and concentration. The number of concentration

measurements is limited by the decrease in mean density taking more and more samples.

Refractive indices and concentrations are used to calculate densities via the Lorentz-Lorenz relation [3/

$$\rho = \frac{n^2 - 1}{n^2 + 2} \frac{M}{LL} \quad (4)$$

where we used linear mixing rules for molar mass  $M$  and Lorentz-Lorenz function  $LL$  according to Heller [4/.

$$M_x = x M_1 + (1-x) M_2 \quad (5)$$

$$LL_x = x LL_1 + (1-x) LL_2 \quad (6)$$

### CHOICE OF PURE FLUIDS AND MIXTURES

Our investigations are concerned with three pure fluids,  $SF_6$ ,  $CO_2$  and  $CHF_3$ .

$SF_6$  is a nearly spherical non-polar molecule while  $CHF_3$  shows a strong dipole moment ( $\mu = 1.65$  D).  $CO_2$  is used for test measurements on our light scattering apparatus, because reliable literature data are available for thermal diffusivity of  $CO_2$ .

For all of our mixtures  $SF_6$  is chosen as one component and  $CO_2$  or  $CHF_3$  as the other one. So we hoped to find a possible influence of polarity on the results of our measurements. The essential data of all pure fluids and mixtures are compiled in Table I. The critical temperatures are determined by observing the reappearance of the meniscus with an accuracy of about 0.02 K.

Table I: Data of pure fluids and binary mixtures

	x mol %	$t_c$ °C	$P_c$ bar	$\rho_c$ g/cm <sup>3</sup>	$n_c$	$M_x$ g/mol	$LL_x$ cm <sup>3</sup> /mol
$CHF_3$	100.0	26.02	48.77	0.527	1.0804	70.01	7.0174
	84.8	23.06	46.31	0.572	1.0830	81.57	7.6750
	70.0	23.01	44.99	0.620	1.0847	92.82	8.3153
	49.7	27.00	43.56	0.673	1.0871	108.26	9.1935
	24.5	34.65	41.40	0.718	1.0884	127.42	10.2838
$CO_2$	0.0	45.57	37.45	0.741	1.0878	146.05	11.3437
	32.0	35.06	45.50	0.696	1.0921	113.39	9.8282
	42.0	31.63	49.10	0.673	1.0932	103.19	9.3546
	67.9	23.51	57.78	0.609	1.0986	76.76	8.1280
	100.0	31.07	73.76	0.468	1.1078	44.00	6.6077

### LIGHT SCATTERING MEASUREMENTS

To test our light scattering apparatus, we measured thermal diffusivity of  $CO_2$  on 3 isotherms, along the saturation line and on the critical isochore. We found very good agreement between our data [5/ and measurements of Becker [6/ as shown in Fig. 3. The mean deviation for measurements along the 25°C isotherm is about 1% only.

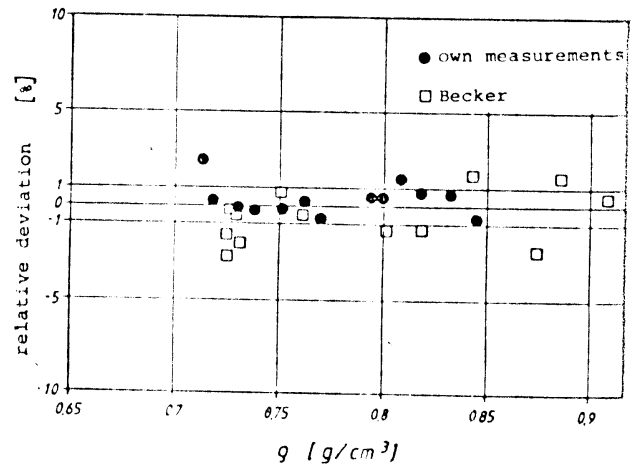


Fig. 3: Thermal diffusivity of  $CO_2$

All our following measurements are restricted to the liquid and gas phase along the saturation line and the critical isochore.

The dependence of thermal diffusivity on temperature is shown for  $SF_6$  in Fig. 4, where it is plotted against  $\tau = 1 - T/T_c$  on a logarithmic scale.

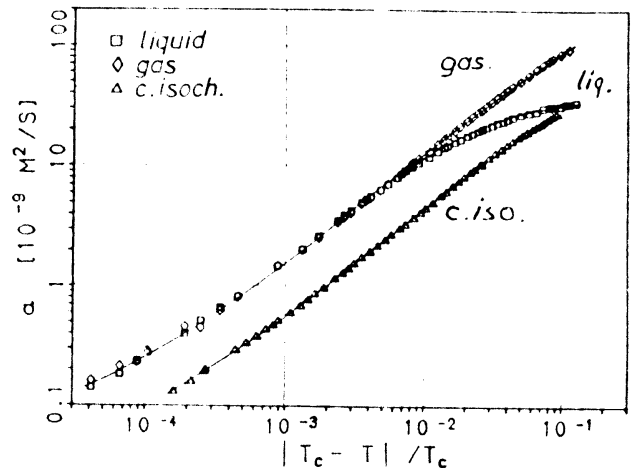


Fig. 4: Thermal diffusivity of  $SF_6$

From this figure we can see that

- thermal diffusivities of liquid and gas phase are nearly identical closer to the critical point than  $\tau = 0.01$
- thermal diffusivities of the gas phase and on the critical isochore can be described by a simple power law according to equation (1) in a temperature range  $3 \cdot 10^{-4} < \tau < 10^{-1}$
- for temperatures  $\tau > 0.01$  the liquid thermal diffusivity shows a strong deviation from the simple power law. This behaviour can be described by a linear dependence of the exponent  $\varphi = \varphi_0 + \tau \varphi_1$

All of our dynamic light scattering experiments are shown in Fig. 5 - 7 for the critical isochore, the saturated gas and the saturated liquid. All pure fluids and binary mixtures show the same temperature dependence. The exponent  $\varphi$  of the power law (1) lies in

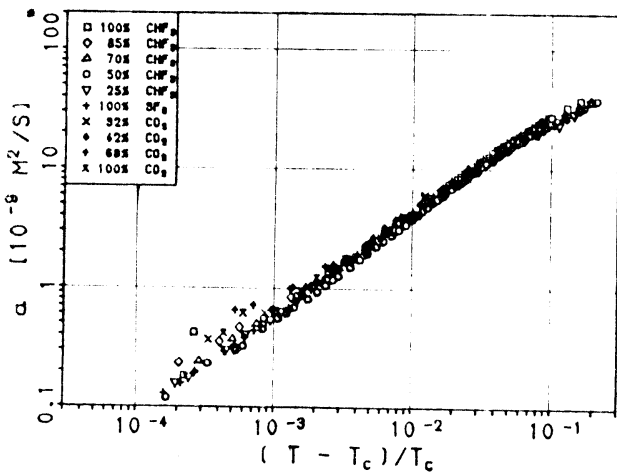


Fig. 5: Thermal diffusivity of critical isochore

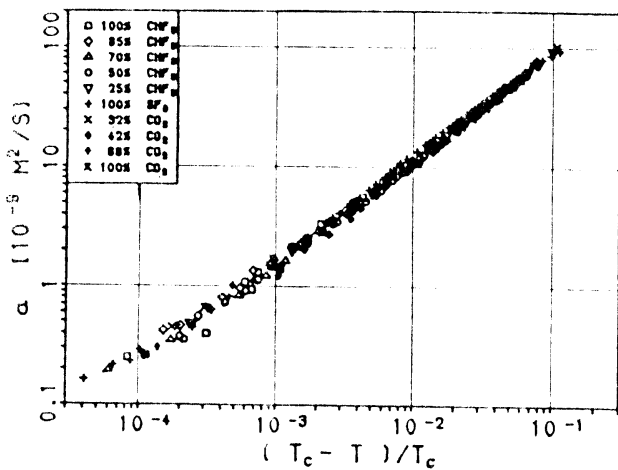


Fig. 6: Thermal diffusivity of saturated gas

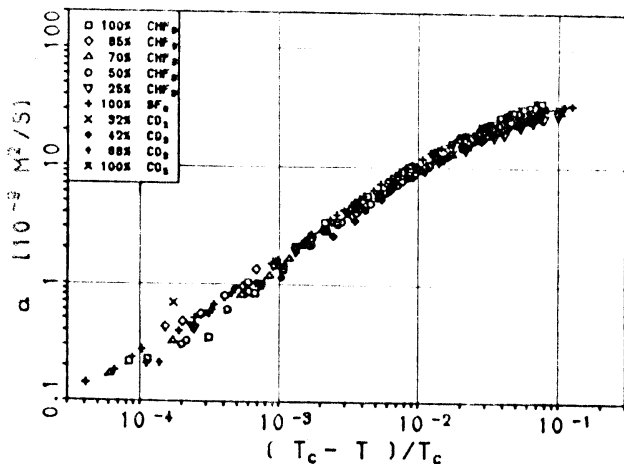


Fig. 7: Thermal diffusivity of saturated liquid

the range of  $\varphi = 0.85 \pm 0.02$  for the gas phases,  $\varphi = 0.87 \pm 0.03$  for the critical isochores and  $\varphi_c = 0.87 \pm 0.06, \varphi_1 = 4.9 \pm 0.4$  for the liquid phases. For both types of mixtures -  $\text{SF}_6 - \text{CO}_2$  and  $\text{SF}_6 - \text{CHF}_3$  - we find a decrease of the coefficient  $\alpha_c$  in (1) below the value for linear mixing of the pure fluid coefficients.

The essential result of these measurements is that no influence of composition and molecular properties on the exponent could be found out.

### CONCENTRATION MEASUREMENTS

Our concentration measurements of the liquid and gas phase should answer the question whether the difference  $x_g - x_l$  of the saturated concentrations can be described according to equation (3) and whether similar exponents  $\beta'$  would occur, for the density coexistence, in pure liquids or binary liquid-liquid mixtures.

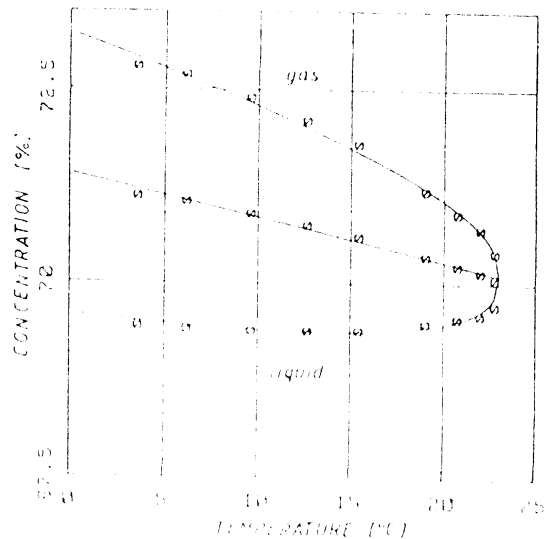


Fig. 8: Saturated concentrations of mixture 30%  $\text{SF}_6$  - 70%  $\text{CHF}_3$

In Fig.8 the result of our measurement is shown for a mixture 30%  $\text{SF}_6$  - 70%  $\text{CHF}_3$ . Here the molar concentration of  $\text{CHF}_3$  is plotted, which is accumulated in the gas phase (upper branch). The lower branch shows concentration of  $\text{CHF}_3$  in the liquid phase. If we assume a linear variation of the rectilinear diameter

$$(x_g + x_l)/2 = \bar{x} + A'(1 - T/T_c) \quad (7)$$

we find parameters  $A'$ ,  $B'$ ,  $\beta'$  as listed in Table II. All of the exponents  $\beta'$  lie in a range of  $0.39 \pm 0.02$ . The real uncertainty of  $\beta'$  is determined to about  $\pm 0.04$  because of the larger scatter of measurements near the critical point. This fact can be seen from a plot of all data in Fig. 9, where  $B'$  (equ.3) is used to reduce measurements to a common scale.

Table II : Parameters of concentration measurements

Mixture	$x_m$ [%]	$\bar{x}$ [%]	$\lambda'$ [%]	$\beta'$ [%]	$\beta'$ -
30% SF <sub>6</sub> - 70% CHF <sub>3</sub>	70.0	70.1	16.9	10.2	0.404
50% SF <sub>6</sub> - 50% CHF <sub>3</sub>	49.7	50.3	36.2	26.5	0.389
75% SF <sub>6</sub> - 25% CHF <sub>3</sub>	25.5	25.3	37.0	60.9	0.821
70% SF <sub>6</sub> - 30% CO <sub>2</sub>	29.5	29.8	52.6	34.3	0.383
58% SF <sub>6</sub> - 42% CO <sub>2</sub>	41.1	41.5	50.0	34.0	0.390
32% SF <sub>6</sub> - 68% CO <sub>2</sub>	67.9	68.3	36.8	24.2	0.388
23% SF <sub>6</sub> - 77% CO <sub>2</sub>	76.5	76.7	14.2	9.7	0.379

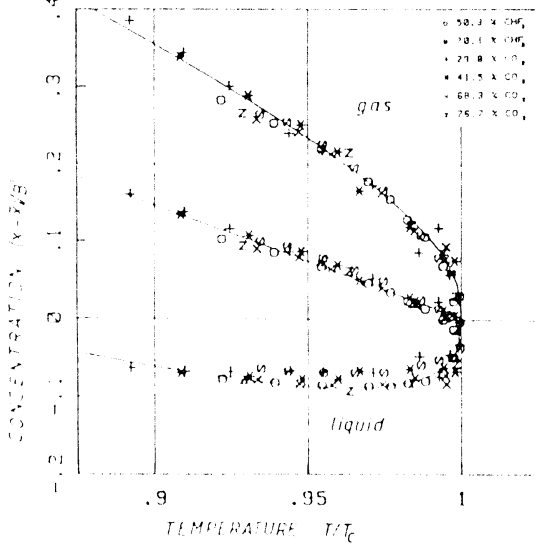


Fig. 9: Reduced concentration measurements

**REFRACTIVE INDEX AND DENSITY**

From refractive index measurements we calculated density according to equations (4) - (6). Fitting this data to equations (2) and (8)

$$(g_l - g_q)/(2g_c) = 1 + \lambda(1-T/T_c) \quad (8)$$

we find the parameters listed in Table III. For all fluids investigated the exponent  $\beta$  of the density coexistence curve lies in a range of  $0.338 < \beta < 0.350$ . Obviously there is no influence of concentration or molecular

Table III : Parameters of density

Mixture	A	$\lambda$	$\beta$
100% CHF <sub>3</sub>	0.796	4.060	0.3462
85% CHF <sub>3</sub>	0.935	3.919	0.3413
70% CHF <sub>3</sub>	0.908	3.916	0.3447
50% CHF <sub>3</sub>	0.786	3.869	0.3469
25% CHF <sub>3</sub>	0.758	3.729	0.3399
100% SF <sub>6</sub>	0.796	3.831	0.3403
32% CO <sub>2</sub>	0.816	3.692	0.3375
42% CO <sub>2</sub>	0.776	3.843	0.3505
68% CO <sub>2</sub>	0.778	3.878	0.3486
100% CO <sub>2</sub>	0.800	3.921	0.3504

properties on the parameters of equations (4) - (6). Fig. 10 shows this behaviour for all 10 pure fluids and mixtures.

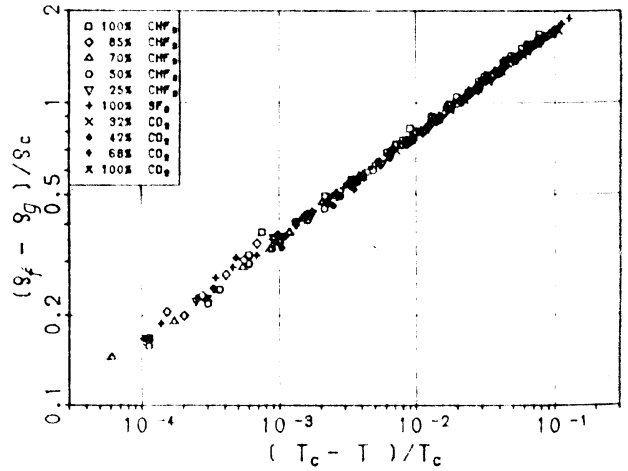


Fig. 10: Reduced density measurements

**DISCUSSION**

In this work we used dynamic light scattering to investigate the decay rate of fluctuations in pure fluids and binary liquid gas mixtures. As for the components of our mixtures the differences in refractive index are very small we are sure that we really measure thermal diffusivity even in the case of the mixtures investigated.

Simultaneously we measured refractive indices and concentrations along the saturation line to calculate density data via the Lorentz-Lorenz relation.

What we found out is that thermal diffusivity, concentration and density can be described by a simple power law in a range of temperatures  $|\Delta T/T_c| < 0.1$ . The exponents of these power laws do not show any dependence on molecular properties or on concentration.

**REFERENCES**

- Berne, B.J., Dynamic Light Scattering, Wiley, New York, (1976)
- Cummins, H.Z. and Pike, E.R., Photon Correlation and Light Beating Spectroscopy, Plenum Press, New York, (1976)
- Rathjen, W. and Straub, J., 7th Symposium on Thermophysical Properties, A. Cezairliyan Ed., American Society of Mechanical Engineers, New York, (1977), p. 889
- Heller, W., J. Phys. Chem. 69, 1123 (1969)
- Reile, F., Thesis, Munich, (1981)
- Becker, H. and Grigull, U., Wärme- und Stoffübertragung 11, 9 (1978)