Evidence of a Liquid-Liquid-Transition in *n*-Tetracosane
The Behavior of the Specific Volume

H. P. Grossmann[1], W. Dollhopf[1] and J. K. Krüger[2]

[1] Abteilung für Angewandte Physik der Universität Ulm, Oberer Eselsberg, D-7900 Ulm,
Federal Republic of Germany

[2] Experimentalphysik, Universität des Saarlandes, Bau 38, D-6600 Saarbrücken,
Federal Republic of Germany

Dedicated to Prof. H.-J. Cantow on the occasion of his 60th birthday

Summary
Dilatometric measurements of n-Tetracosane from 330 K up to 420 K are
reported. These experiments show evidence for a small kink in the specific
volume – temperature curve. The correct statistical interpretation of the
measured data yield a discret transition temperature above the melting
point at about 378 K in close agreement with the results from other experi-
mental methods.

Introduction
The occurrence of transition like phenomena in n-alkane melts were already
discussed by MOORE et al. (1953) and BALTA-CALLEJA et al. (1976). They dis-
cussed their observation in terms of a transition from a smectic - like into
a disordered liquid. KRÜGER (1979) reported first evidences for a transition
by Brillouin-spectroscopic investigations and found a transition temperature
of $T_u \approx 110\ °C$ in close agreement with the results of BALTA-CALLEJA. However
the n-alkane melt became not mesomorphic (FISCHER et al. (1979)). Because
of the lack of a satisfactory explanation of the origin of T_u the notion of
local mesomorphic order was introduced (KRÜGER et al. (1980a)). Later on in-
vestigations with other physical methods and on other n-alkanes PIETRALLA
et al. (1980), KRÜGER et al. (1980b), KRÜGER et al. (1981a) seemed to con-
firm the existence of a discrete and prominent temperature T_u in n-Tetra-
cosane and other n-alkanes. However, the existence of T_u is not generally
accepted (e.g. FISCHER, 1979, 1980; SNYDER, 1982; HÖHNE, 1981; CLAUDY and
LÉTOFFÉ, 1983). Especially the behaviour of the specific heat around T_u has
been a recent subject of controversy (DENNY and BOYER, 1981; HÖHNE, 1981;
CLAUDY and LÉTOFFÉ, 1983; KRÜGER et al., 1983): either there is no anomaly
of the specific heat at all at T_u or the effect is so small that it cannot
be resolved with DSC- or DTA-methods. The last mentioned possibility seems
to be reasonable at a weak liquid-liquid transition. Indeed, all physical
parameters which reflect T_u depend only slightly on temperature and there-
fore the determination of T_u requires a <u>great precision of measurement</u> and
a <u>correct statistical interpretation</u> of the measured data (KRÜGER et al.
(1981b).

Experimental
The specific volume of n-Tetracosane was determined with a dilatometer
developed in our laboratory (DOLLHOPF, 1978; LEUTE et al., 1976). The
apparatus used was a pressure dilatometer consisting of a piston-cylinder
device of 22 mm diameter. For the measurements reported in this paper the
pressure was kept constant at 9 bar by a weight attached on the movable
piston. The expansion of the probe leads to a diplacement of the piston.
This change in the length of the specimen was directly measured. The data
obtained in this way are in the following called "non calibrated data".

They could be determined with a relative error smaller than 10^{-4}. The specific volume (fig.1a) thus can be determined from this length and the constant diameter of the cylinder taking into account the thermal expansion of the dilatometer itself. The dilatometer was heated electrically and the temperature was measured close to specimen with a thermocouple within an accuracy of $0.1\,K$. However, the absolute temperature is correct only within $\pm 1\,K$.

Results and discussion

The specific volume of the melt of n-Tetracosane was determined by two runs as a function of temperature. Fig.1a shows the results for data set 1.
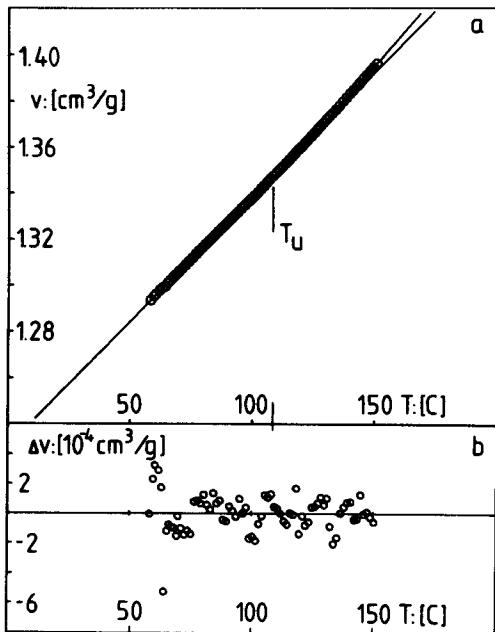

Fig. 1: a) Specific volume v of n-Tetracosane as a function of temperature (data set 1).

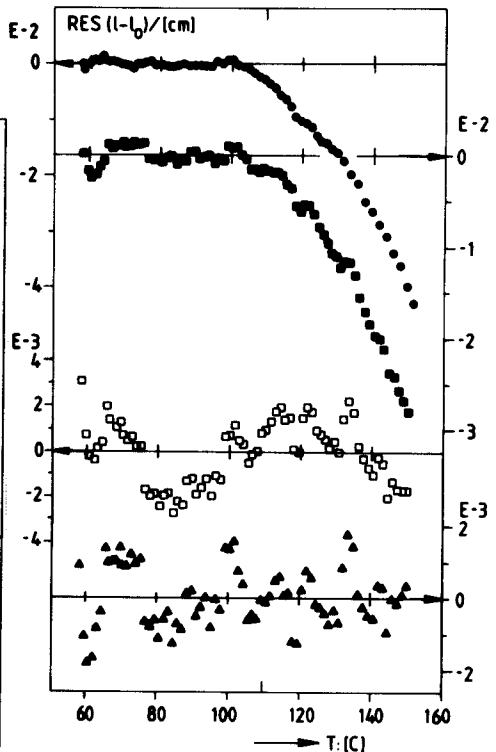b) Residuals v as function of temperature (explanation see text).

Fig. 2: Residuals of the non-calibrated specific volume data versus temperature for different fit functions and fit conditions (explanation see text).

The two non calibrated data sets were fitted by the method of least squares to different types of continous functions. Fig.2 shows the residuals of some of these fits. The upper two curves display the residuals of data set 1 and 2 under the condition that the data between about 60 °C and 90 °C were fitted to a straight line (■ data set 1, ● data set 2). It is obvious that a straight line discribes the data sets well up to about 105 °C . Above 105 °C a significant and systematic deviation of the residuals from zero

occurs.

There is obviously no physical reason to describe the specific volume by only one straight line. On the other hand no discontinuities are expected in the volume expansion coefficient – temperature curve if not a transition like phenomenon occurs. Therefore, we have fitted the two non calibrated data sets also with polynominal functions of different orders.

The third curve from above of fig.2 (□) displays the residuals of data set 2 for a polynominal of 2nd order. It is clear from the systematic distribution of the residuals (lumpy distribution) that a polynominal of 2nd order doesn't describe the data set satisfactorily from a statistical point of view. The data sets were also fitted to the combination of two polynominals which are inclined at a temperature T_u (eq. 1):

$$(1) \quad v(T) = \frac{1}{2} v_o \left[v_1(T) + v_2(T) \right] = \begin{cases} \frac{1}{2} v_o v_1 \quad , \quad T < T_u \\ \frac{1}{2} v_o v_2 \quad , \quad T > T_u \\ \\ v_o \quad \quad , \quad T = T_u \end{cases}$$

with

$$(2) \quad v_1(T) = \left[\text{sign}(T_u - T) + 1 \right] \left[1 - c_1(T_u - T) - c_2(T_u - T)^2 \right]$$

$$(3) \quad v_2(T) = \left[\text{sign}(T - T_u) + 1 \right] \left[1 - c_3(T - T_u) - c_4(T - T_u)^2 \right]$$

The residuals belonging to the non calibrated data set 2 are shown in the lower curve of fig.2 (▲). Only a polynominal function of 6th order leads to a comparable small sum of squares and a statistical distribution of the residuals. It should be mentioned that eq. 1 contains the temperature T_u at which v(T) has a bent as a fitting parameter. The parameter c_2 is found to be nearly zero for both data sets and can be omitted. As a consequence the specific volume as a function of temperature below T_u can be described satisfactorily by a straight line. Above T_u a polynominal of second order is adequate for the description of the data. The estimates for the two data sets are:

	set 1		set 2		average
v_o:	1.347	± 0.004	1.339	± 0.002	1.343
c_1:	$8.04 \cdot 10^{-4}$	$\pm 0.02 \cdot 10^{-4}$	$7.93 \cdot 10^{-4}$	$\pm 0.01 \cdot 10^{-4}$	$7.985 \cdot 10^{-4}$
c_2:	$9.3 \cdot 10^{-9}$	$\pm 6 \cdot 10^{-9}$	$5.2 \cdot 10^{-9}$	$\pm 4 \cdot 10^{-9}$	$7 \cdot 10^{-9}$
c_3:	$8.22 \cdot 10^{-4}$	$\pm 0.09 \cdot 10^{-4}$	$8.15 \cdot 10^{-4}$	$\pm 0.05 \cdot 10^{-4}$	$8.2 \cdot 10^{-4}$
c_4:	$9 \cdot 10^{-7}$	$\pm 1 \cdot 10^{-7}$	$9.7 \cdot 10^{-7}$	$\pm 0.2 \cdot 10^{-7}$	$9.4 \cdot 10^{-7}$
T_u:	108	± 4	101	± 4	105
Σ^2:	$1.1 \cdot 10^{-6}$		$3.6 \cdot 10^{-7}$		
σ:	$1.3 \cdot 10^{-4}$		$7.8 \cdot 10^{-5}$		

where Σ^2 corresponds to the sum of squares and σ to the standard deviation.

v_o and c_1 of the 1st and 2nd data set differ only slightly more from each other than allowed by the appropriate error intervals. The volume expansion coefficient α at T_u ($\lim_{T \to T_u - \varepsilon} \alpha(T) = c_1$ and $\lim_{T \to T_u + \varepsilon} \alpha(T) = c_3$) changes disconti-nuously for both data sets by the amount of $\Delta\alpha = 0.2 \cdot 10^{-4} \ K^{-1}$ which is far outside the margin of error. T_u is in agreement with those found from other measurements like sound velocity, viscosity, longitudinal relaxation time and magnetic susceptibility. It therefore seems reasonable to believe in the existence of a discrete and prominent temperature T_u in n-Tetracosane. If static physical properties change spontaneously at a fixed temperature one usually believes in transition like phenomena at this temperature.

Indeed, the specific volume about T_u behaves very similar as e.g. the specific volume behaves at the glass transition temperature T_g of polymers. It should also be mentioned that the present results about the specific volume at T_u agree with results for PE 6600 indirectly determined by Brillouin-spectroscopy: KRÜGER (1980a); KRÜGER (1981a). The volume expansion coefficient α is smaller below T_u than above T_u. This behaviour is opposite to the behaviour of the sound velocity gradient δ above and below T_u: KRÜGER (1979). As for the case of PE 6600 a discontinous change of the Grüneisenparameter $\gamma_{\vec{q},\vec{P}}$ has been estimated:

(4) $\qquad \gamma_{\vec{q},\vec{P}} \simeq \delta \cdot \alpha^{-1}$

$\vec{q}$ and $\vec{P}$ are the wavevector and the polarization vector of the sound wave, respectively. The values for δ below and above T_u are taken from the Brillouin-data (KRÜGER, 1979).

(5) $\qquad \gamma_{\vec{q},\vec{P}} = \begin{cases} 3.9, & T < T_u \\ 2.9, & T > T_u \end{cases}$

This implies that the anharmonicity of the molecular interaction forces changes substantially at the temperature T_u supporting the idea of a transition like phenomen at T_u. Although we believe now in the existence of a transition at T_u the origin of this transition is completely unclear. As mentioned above a transition into an ordinary liquid crystalline state is unlikely. Another kind of intermolecular long range order also seems not to exist: e.g. FLORY (1979). One may speculate that at T_u an intra-molecular transition takes place from a random coil conformation ($T > T_u$) in a very disturbed helix like conformation ($T < T_u$) (GROSSMANN, 1981) under retaining the straight helix axis, as was proposed earlier by KRÜGER (1981). Another possible explanation could be a transition of the superstructural blocks in the oligomeric melt (PECHHOLD et al., 1979). In order to decide whether the transition at T_u is a superstructural effect or an effect of short range order, further experiments (hypersonic investigations (KRÜGER, 1983b), n-scattering experiments (SAUTTER, 1983) etc. are planned) have to be carried out.

Acknowledgement

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