Measurements on n- and Isobutane Using a Vibrating-Wire Viscometer and Correlations of Their Viscosity Surfaces Using a Structure-Optimisation Method

S. Herrmann[1,3], E. Vogel[2], E. Hassel[3], R. Span[4]

[1]Fachgebiet Technische Thermodynamik, Hochschule Zittau/Görlitz

[2]Institut für Chemie, Universität Rostock

[3]Lehrstuhl für Technische Thermodynamik, Universität Rostock

[4]Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum

Thermophysical Properties for Technical Thermodynamics

27th of March, 2013, Rostock

Hochschule Zittau/Görlitz UNIVERSITY OF APPLIED SCIENCES — Studienstiftung des deutschen Volkes — Universität Rostock Traditio et Innovatio

Outline

Motivation and Tasks

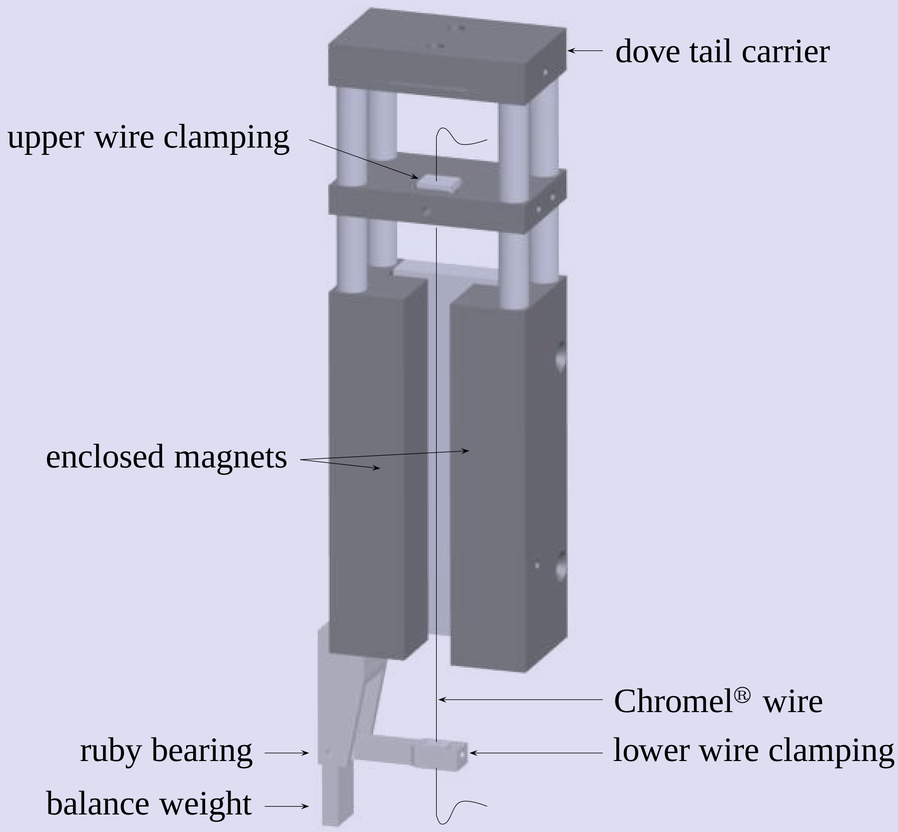
Motivation

- n-Butane and isobutane
  – industrially and ecologically important fluids

Tasks

- Measurement of new precise $\eta\rho pT$ data in large temperature and pressure ranges and in the near-critical region
- Generation of viscosity-surface correlations for n- and isobutane using the structure-optimisation method by Setzmann and Wagner

Vibrating-Wire Viscometer



- Wire:
  $L_W = 9$ cm
  $f = 280$ Hz
  $D = 25\ \mu$m
  Ni90/Cr10
- Magnets:
  $L_M = 6$ cm
  Sm_2Co_{17}

Vibrating-Wire Viscometer

Implementation

1. Initialization of a vibration of the clamped wire in a homogeneous magnetic field by means of a sinusoidal voltage pulse
2. Magnetic induction of a voltage in the moving wire
3. Detection of the damped harmonic oscillation via measuring the voltage as function of time
4. Determination of the logarithmic decrement and of the frequency using a non-linear fit
5. Iterative calculation of the viscosity including the density measured simultaneously

Calibration

- Iterative adjustment of the wire radius by comparing the viscosity in the limit of zero density of a measurement on helium with a theoretically calculated value (Bich *et al.*, 2007)

Single-Sinker Densimeter

Implementation

- Use of the buoyancy principle of Archimedes (Ruhr-Universität Bochum, Brachthäuser *et al.*, 1993)
- Difference between the weight in vacuo and the weight under the influence of the buoyancy force on the sinker due to the fluid
- Calibration of the balance and determination of the sinker volume
- Density of the fluid:

$$\rho = \frac{m_{\mathrm{s,vac}}(T) - m_{\mathrm{s,fluid}}(T,p)}{V_{\mathrm{s}}(T,p)}$$

- Magnetic-suspension coupling (Lösch, 1987):
  Contactless power transmission from the measuring cell to the balance situated under ambient conditions

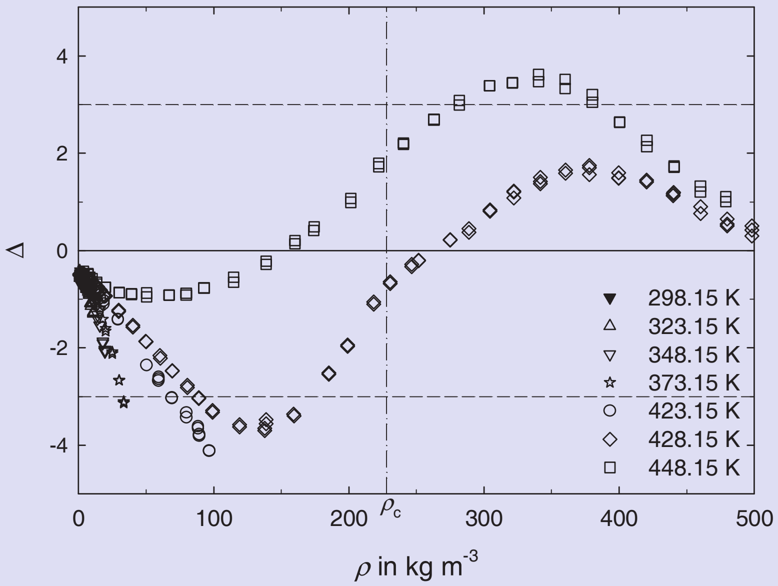
Combined Viscosity-Density Measuring System

Results and Comparisons

Viscosity of n-Butane

Comparison of the new data η_{exp} with η_{cor} of Vogel *et al.*[1]
Uncertainty of the new data: $\Delta\eta/\eta \leq 0.5\%$

- Deviations up to $\pm 4\%$



$$\Delta = 100\,\frac{\eta_{exp} - \eta_{cor}}{\eta_{cor}}$$

$$T_c = 425.125 \text{ K}$$
$$p_c = 3.796 \text{ MPa}$$
$$\rho_c = 228.0 \text{ kg m}^{-3}$$

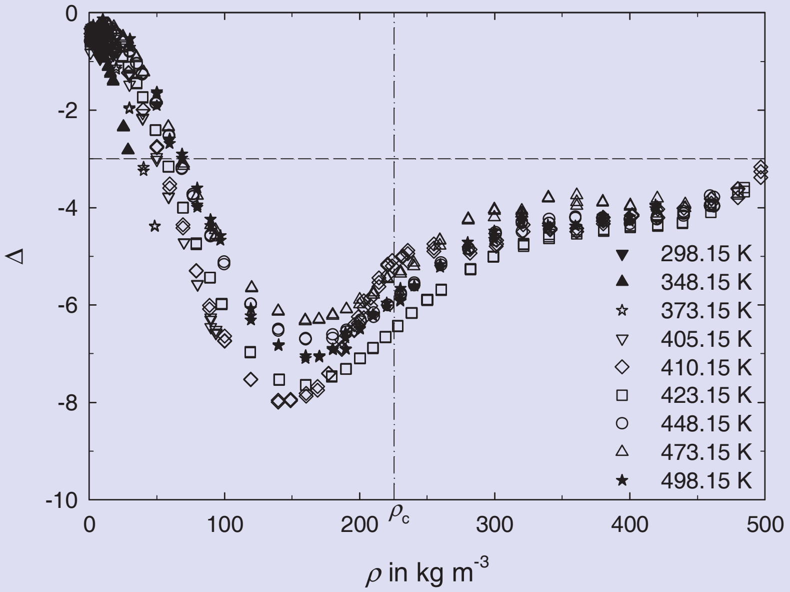
[1] Vogel, E.; Küchenmeister, C.; Bich, E.: *High Temp.-High Pressures* **31**, 173-186 (1999).

Results and Comparisons

Viscosity of Isobutane

Comparison of the new data η_{exp} with η_{cor} of Vogel *et al.*[2]
Uncertainty of the new data: $\Delta\eta/\eta \leq 0.5\%$

- Deviations down to -8%



$$\Delta = 100\,\frac{\eta_{exp} - \eta_{cor}}{\eta_{cor}}$$

$$T_c = 407.81\ \text{K}$$

$$p_c = 3.629\ \text{MPa}$$

$$\rho_c = 225.5\ \text{kg m}^{-3}$$

[2] Vogel, E.; Küchenmeister, C.; Bich, E.: *Int. J. Thermophys.* **21**, 343-356 (2000).

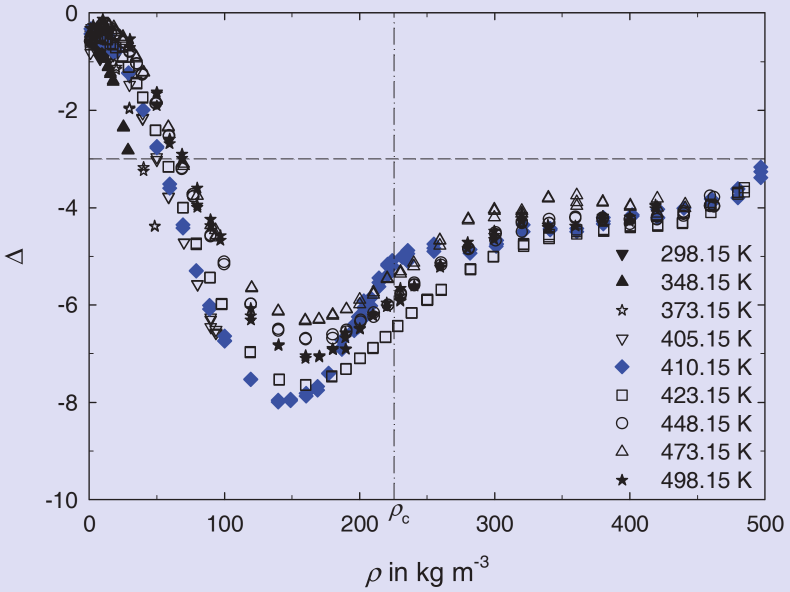
Viscosity Measurements Results of the Measurements

Results and Comparisons

Viscosity of Isobutane

Comparison of the new data η_{exp} with η_{cor} of Vogel *et al.*[2]
Uncertainty of the new data: $\Delta\eta/\eta \leq 0.5\%$

- Deviations down to -8%



$$\Delta = 100\,\frac{\eta_{exp} - \eta_{cor}}{\eta_{cor}}$$

$$T_c = 407.81\ \text{K}$$

$$p_c = 3.629\ \text{MPa}$$

$$\rho_c = 225.5\ \text{kg m}^{-3}$$

[2] Vogel, E.; Küchenmeister, C.; Bich, E.: *Int. J. Thermophys.* **21**, 343-356 (2000).

Correlation Method Using Structure Optimisation

Selection Criteria

- Feasibility of combination of different terms
- Requirement of reliable experimental data
- Use of simple functional dependencies, e.g., $\eta = \eta(T, \rho)$
- Successful viscosity-surface correlations for propane[3] and R134a[4] $\rightarrow$ Scalabrin *et al.*

Procedure

- Evaluation and classification of all available viscosity data
- Selection of terms for the complete fluid range of thermodynamic states including the near-critical region
- Assessment of the resulting correlation using statistical parameters and adequate description of experimental data

[3] Scalabrin, G.; Marchi, P.; Span, R.: *J. Phys. Chem. Ref. Data* **35**, 1415-1442 (2006).
[4] Scalabrin, G.; Marchi, P.; Span, R.: *J. Phys. Chem. Ref. Data* **35**, 839-868 (2006).

Selection of the Variables

Choice of $\eta = \eta(T, \rho)$ instead of $\eta = \eta(p, T)$

Viscosity Data from the Literature

- Problem: most of the data given as $\eta(p, T)$
- Calculation of density from p and T using current equations of state by Bücker and Wagner[5] for n-butane and isobutane
  $\rightarrow$ correlation of $\eta(T_{\text{exp}}, \rho_{\text{cal}})$ with $\rho_{\text{cal}}(p_{\text{exp}}, T_{\text{exp}})$ in the case that no experimental density data available

New Viscosity Data

- New data of this work given as $\eta(T_{\text{exp}}, \rho_{\text{exp}})$ resulting from simultaneous determination of viscosity and density

[5] Bücker, D.; Wagner, W.: *J. Phys. Chem. Ref. Data* **35**, 929-1019 (2006).

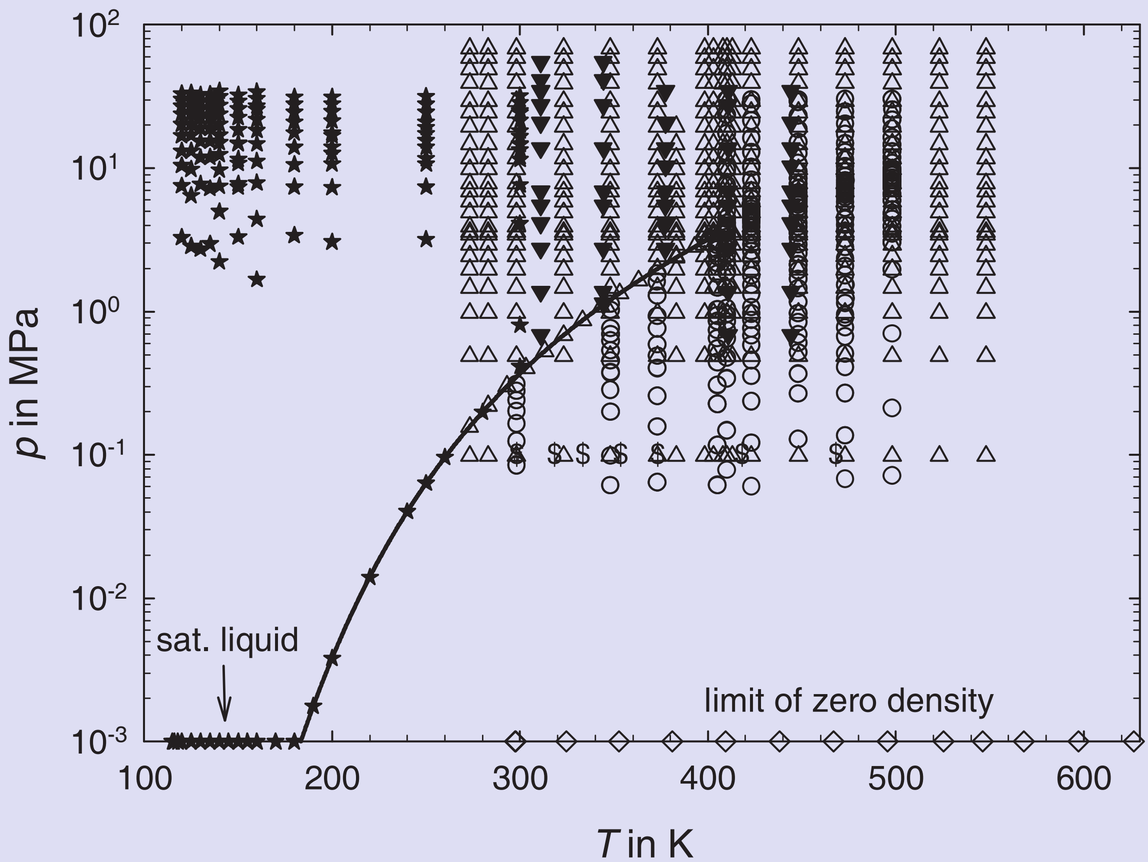
Selection of the Terms

- Selection of terms for different fluid regions
  1. Viscosity in the limit of zero density $\eta_0(T) \rightarrow \sum_i A_{i0}\tau^i\delta^0$
  2. Residual viscosity $\eta_\mathrm{f}(T,\rho) + \eta_\mathrm{h}(T,\rho)$
     - $\eta_\mathrm{f}(T,\rho) \rightarrow \sum_{i=0}^{8}\sum_{j=1}^{15} A_{ij}\tau^i\delta^j$
     - $\eta_\mathrm{h}(T,\rho) \rightarrow \sum_{k=1}^{5} A_k \frac{\delta}{\delta_{0k}(\tau)-\delta}$

       with $\delta_{0k}(\tau) = B_k\left(1+\sum_{l=1}^{5} C_{kl}\tau^{\frac{l}{2}}\right)$
  3. Near-critical region $\eta_\mathrm{c}(T,\rho) \rightarrow \gamma e^{-\beta(\delta-1)^2}\sum_{m=1}^{3}\frac{A_m}{(\tau-1)^m}$
- Reduced quantities: $\tau = \frac{T}{T_\mathrm{c}}$, $\delta = \frac{\rho}{\rho_\mathrm{c}}$, $\beta = \frac{\rho_\mathrm{c}}{D}$
- Bank of terms for the correlation:

$$\frac{\eta_\mathrm{bank}(T,\rho)}{\mu\mathrm{Pa\ s}} = \frac{\eta_0(T)}{\mu\mathrm{Pa\ s}}A_0 + \sum_{i=0}^{8}\sum_{j=1}^{15} A_{ij}\tau^i\delta^j + \sum_{k=1}^{5} A_k\frac{\delta}{\delta_{0k}(\tau)-\delta} + $$
$$+\gamma e^{-\beta(\delta-1)^2}\sum_{m=1}^{3}\frac{A_m}{(\tau-1)^m}$$

Isobutane – Primary Data in a p-T Diagram



Isobutane — Viscosity-Surface Correlation

Correlation

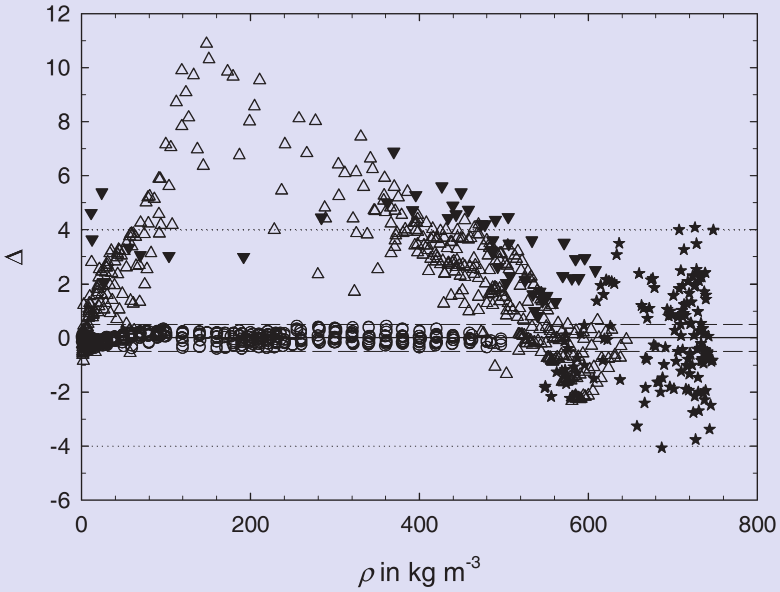
- Equation with 12 terms (n-butane: 11 terms)
- Viscosity in the limit of zero density integrated in the first sum
- Three (n-butane: two) terms accounting for the high-viscosity values in the liquid region
- One term accounting for the critical enhancement

$$\frac{\eta_{\mathrm{cor,i-C_4H_{10}}}(T,\rho)}{\mu\mathrm{Pa\ s}} = \sum_{i=1}^{8} A_i \tau^{t_i} \delta^{d_i} + \sum_{i=9}^{11} A_i \frac{\delta}{\delta_{0i}(\tau) - \delta} + \gamma e^{-\beta(\delta-1)^2} \frac{A_{12}}{\tau - 1}$$

$$\text{with} \quad \delta_{0i}(\tau) = B_i \left(1 + C_{i1}\tau^{\frac{1}{2}}\right), \qquad \beta = \frac{\rho_c}{D}$$

Isobutane — Deviations from Experimental Data

- Large deviations at low and high densities



$$\Delta = 100\,\frac{\eta_{\mathrm{exp}} - \eta_{\mathrm{cor}}}{\eta_{\mathrm{cor}}}$$

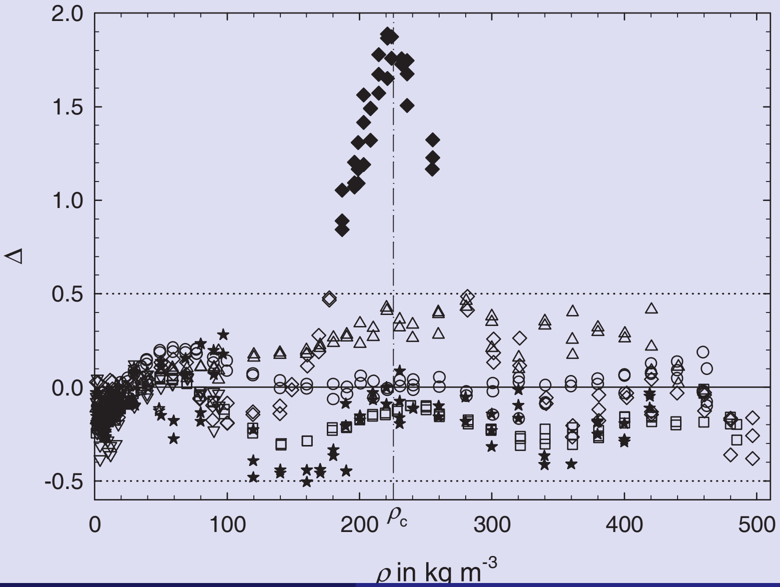
▼,△,★ experimental data from the literature

○ new experimental data

Isobutane — Deviations from Experimental Data

Deviations from a preliminary correlated equation without a term accounting for the critical enhancement of the viscosity

- Evident critical enhancement of viscosity
- Amount of critical enhancement ($< +2\%$) corresponding to predictions from theory



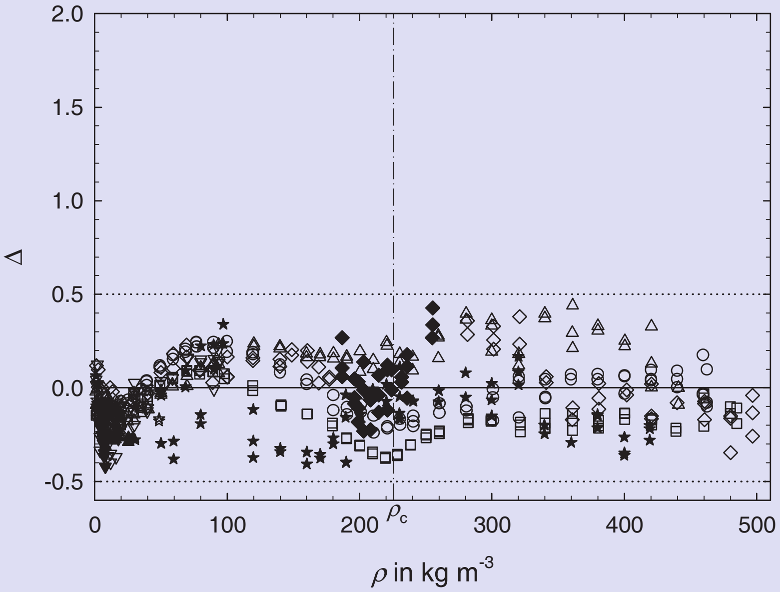
$$\Delta = 100\,\frac{\eta_{\mathrm{exp}} - \eta_{\mathrm{cor,prel}}}{\eta_{\mathrm{cor,prel}}}$$

◆ data influenced by the near-critical region at 410.15 K

Isobutane — Deviations from Experimental Data

Deviations from the correlated equation for isobutane including a term accounting for the critical enhancement of the viscosity

- Deviations up to ± 0.5 %



$$\Delta = 100\,\frac{\eta_{\mathrm{exp}} - \eta_{\mathrm{cor}}}{\eta_{\mathrm{cor}}}$$

◆ data influenced by the near-critical region at 410.15 K

Conclusion and Outlook

- New precise viscosity and density data were simultaneously measured using a vibrating-wire viscometer and a single-sinker densimeter
- New viscosity-surface correlations were generated for n-butane and isobutane based on new precise experimental viscosity data
- The structure-optimisation method of Setzmann and Wagner (Ruhr-Universität Bochum) was used
- The viscosity was correlated as $\eta(T, \rho)$
- One term accounting for the critical enhancement was included in the representation of the viscosity surfaces
- The viscosity of the liquid phase is well described

- Further work on ethane and propane

$\rightarrow$ precise data using the vibrating-wire viscometer are available for both fluids

Thank You for Your Attention!