A New Viscosity-Surface Correlation for Propane

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   - Problems with consistency
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Motivation – Problems and Tasks

Convenience for engineers

- Use of a Standard Database Program for Thermophysical Properties – consistent with respect to thermodynamic and transport properties: REFPROP[1]
- Consistency of the formulations for water:
  - Equation of state (EOS): Wagner and Pruss (2002)[2]
  - Viscosity η: Huber *et al.* (2009)[3]
  - Thermal conductivity λ: Huber *et al.* (2012)[4]
- Ethane: EOS, η, λ – inconsistent
  - Problem partly solved → new viscosity-surface correlation: presented at the ECTP Conference in Porto, Portugal, last year
  - Paper submitted to *J. Phys. Chem. Ref. Data*

1 Lemmon, E. W., Huber, M. L., and McLinden, M. O., Standard Reference Data Program, National Institute of Standards and Technology, Gaithersburg (2013).

2 Wagner, W. and Pruss, A., *J. Phys. Chem. Ref. Data* **31**, 387-535 (2002).

3 Huber, M. L., Perkins, R. A., Laesecke, A., Friend, D. G., Sengers, J. V., Assael, M. J., Metaxa, I. M., Vogel, E., Mares, R. and Miyagawa, K., *J. Phys. Chem. Ref. Data* **38**, 101-125 (2009).

4 Huber, M. L., Perkins, R. A., Friend, D. G., Sengers, J. V., Assael, M. J., Metaxa, I. M., Miyagawa, K., Hellmann, R. and Vogel, E., *J. Phys. Chem. Ref. Data* **41**, 1-23 (2012).

Problems with consistency

Propane: EOS, η, λ – inconsistent

- Correlations recommended in REFPROP
  - EOS: Lemmon *et al.* (2009)[5]
  - η: Vogel *et al.* (1998)[6]
  - λ: Marsh *et al.* (2002)[7]
- Characterization
  - EOS: classical including the critical region, an additional parametric crossover EOS not needed
  - η: not including a critical enhancement, but using an old-fashioned classical MBWR
  - λ: including a critical enhancement according to a simplified crossover model by Olchowy and Sengers (1988)[8], but again based on an old-fashioned classical MBWR

5 Lemmon, E. W., McLinden, M. O., and Wagner, W., *J. Chem. Eng. Data*, **54**, 3141-3180 (2009).

6 Vogel, E., Küchenmeister, C., Bich, E., and Laesecke, A., *J. Phys. Chem. Ref. Data*, **27**, 947-970 (1998).

7 Marsh, K., Perkins, R., and Ramires, M. L. V., *J. Chem. Eng. Data*, **47**, 932-940 (2002).

8 Olchowy, G. A. and Sengers, J. V., *Phys. Rev. Lett.*, **61**, 15-18 (1988).

Correlation method using structure optimization

Selection criteria

- Combination of different terms
- Requirement of reliable experimental data
- Use of simple functional dependencies, e.g., $\eta = \eta(T, \rho)$
- Viscosity-surface correlation for propane[9] (2006) of Scalabrin *et al.* $\rightarrow$ not recommended within REFPROP

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

[9] Scalabrin, G., Marchi, P., and Span, R., *J. Phys. Chem. Ref. Data* **35**, 1415-1442 (2006).

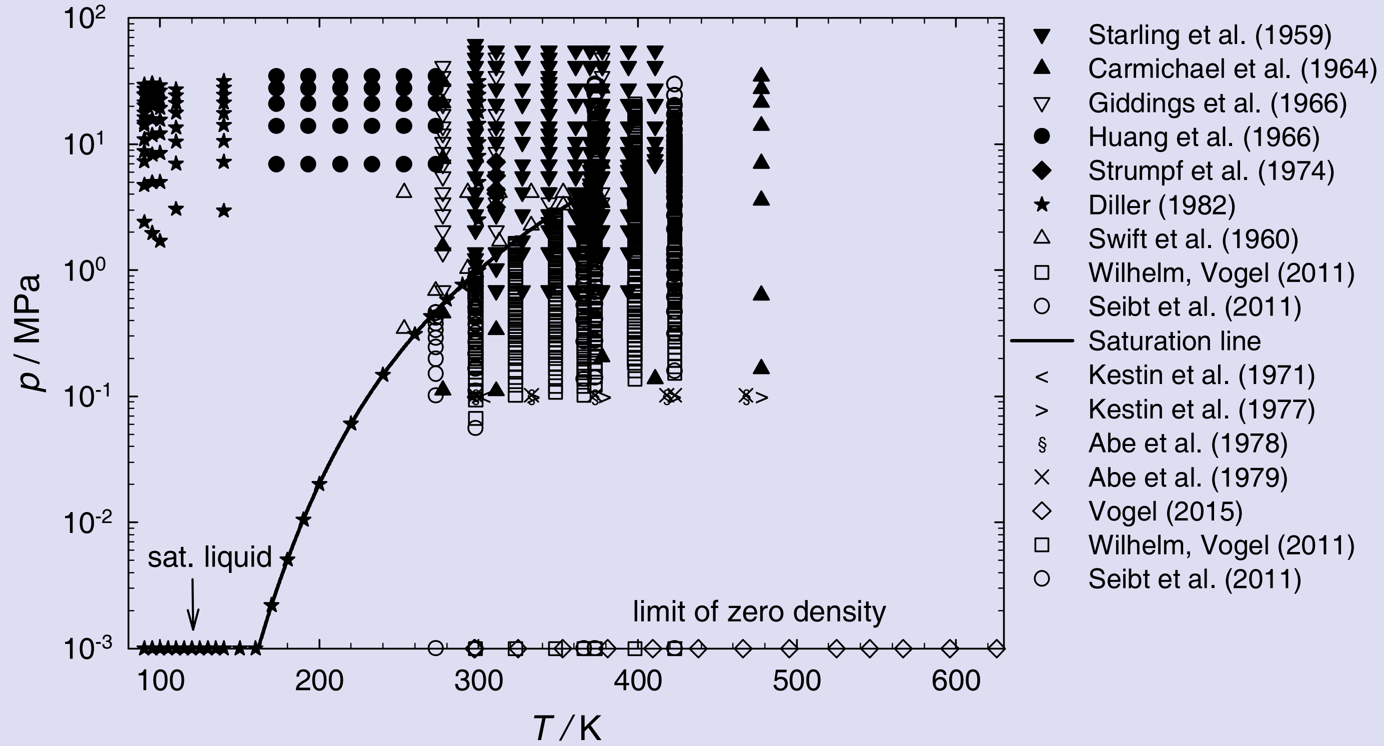
Propane – Primary Experimental Viscosity Data

Authors	Year	Method[10]	Number of points	T K	ρ kg m^{-3}	$\Delta\eta/\eta$ %
Vogel	2015[11]	OD	14	297–625	0	0.3
Wilhelm, Vogel	2011[11]	VW	7	298–423	0	0.3
Seibt *et al.*	2011	VW	5	273–423	0	0.3
Kestin *et al.*	1971	OD	2	296–303	2	0.4
Kestin *et al.*	1977	OD	5	299–478	1–2	0.4–1.0
Abe *et al.*	1978	OD	5	298–468	1–2	0.4–1.0
Abe *et al.*	1979	OD	6	298–468	1–2	0.4–1.0
Starling *et al.*	1959	C	141	298–411	10–578	2.5
Swift *et al.*	1960	FC	13	243–363	330–566	2.5
Carmichael *et al.*	1964	RC	22	278–478	2–567	2.5
Giddings *et al.*	1966	C	74	278–378	10–577	2.5
Huang *et al.*	1966	FC	30	173–273	540–662	2.5
Strumpf *et al.*	1974	OQC	5	311	479–491	2.5
Diller	1982	OQC	84	90–300	489–737	2.5
Wilhelm, Vogel	2011[11]	VW	589	298–423	1–447	0.7
Seibt *et al.*	2011	VW	181	273–423	1–473	0.5

[10] C, capillary; FC, falling cylinder; OD, oscillating disk; OQC, oscillating quartz crystal; RC, rotating cylinder; VW, vibrating wire

[11] re-evaluated data

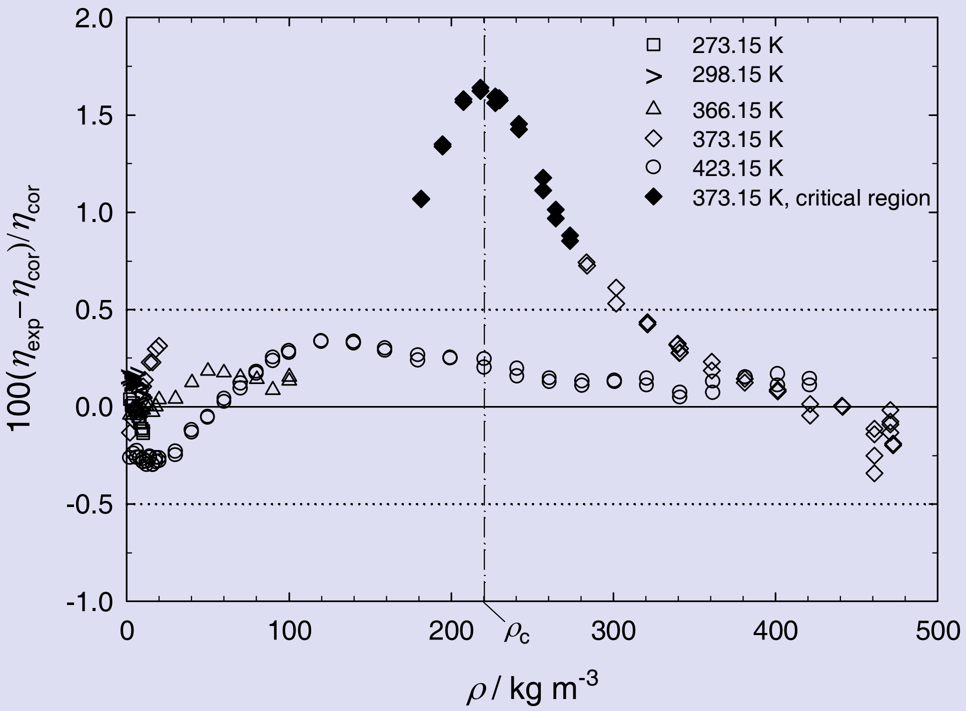
Propane — p, T diagram with primary experimental data



Propane — Correlation without critical enhancement

New data for propane of Seibt *et al.* (2011)[12]

- Deviations up to +1.64 % near critical density ($\rho_c = 220.478$ kg m^{-3})



12 Seibt, D., Voß, K., Herrmann, S., Vogel, E., Hassel, E., *J. Chem. Eng. Data*, **56**, 1476-1493 (2011).

Critical enhancement according to Bhattacharjee *et al.* (1981)[13]

- Viscosity η corresponds to an asymptotic power-law divergence:

$$\eta \approx \eta_b (Q_0 \xi)^{z_\eta} \ .$$

- Critical enhancement represents a multiplicative anomaly:

$$\eta_c = \eta_b [(Q_0 \xi)^{z_\eta} - 1] \ .$$

- Crossover is needed $\longrightarrow$ complete global solution by Olchowy and Sengers (1988) for the mode-coupling theory:

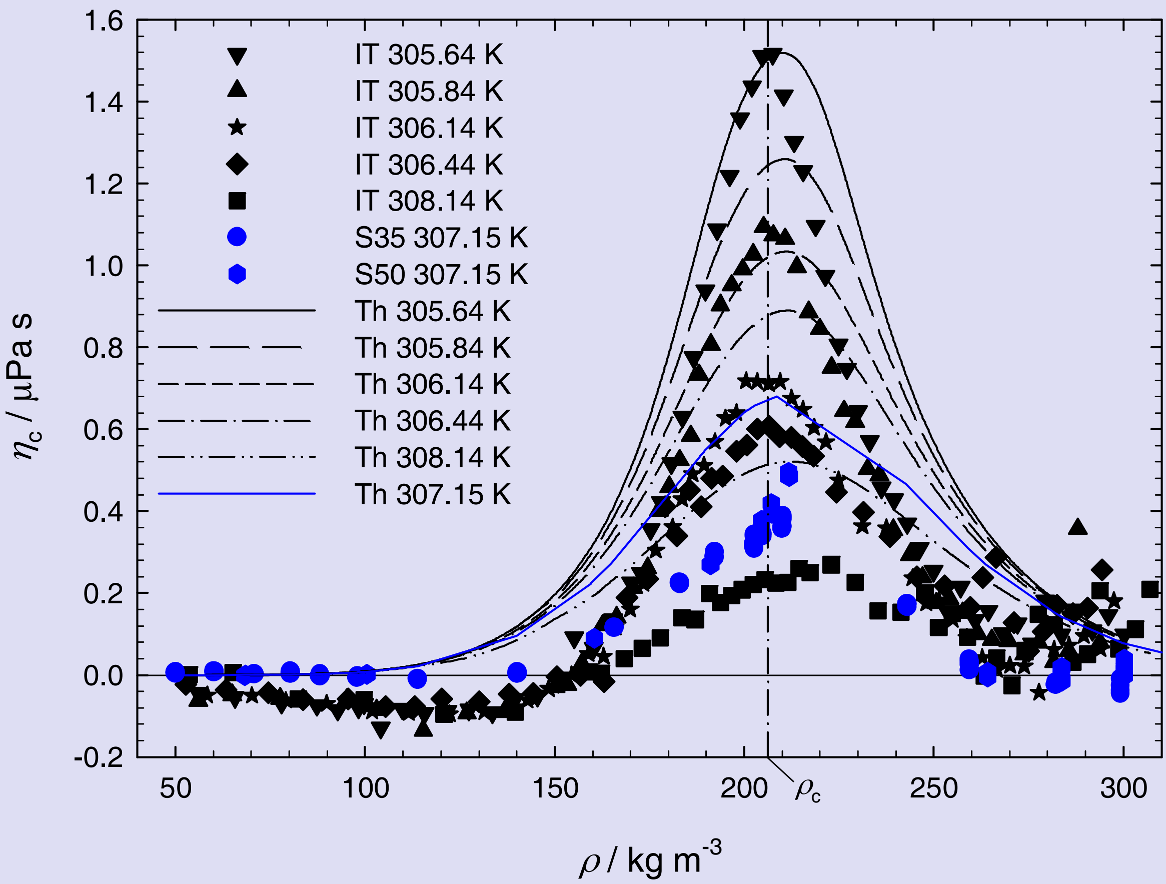
$$\eta_c = \eta_b [\exp(z_\eta H) - 1] \ .$$

- Simplified closed-form solution earlier developed (Bhattacharjee *et al.*) $\longrightarrow$ recently used for IAPWS water (Huber *et al.*, 2009):

$$\eta_c = \eta_b [\exp(z_\eta Y) - 1] \ .$$

[13] Bhattacharjee, J. K., Ferrell, R. A., Basu, R. S., and Sengers, J. V., *Phys. Rev. A* **24**, 1469-1475 (1981).

Critical enhancement – ethane: theory vs. experiment



Viscosity-surface correlation for propane

- Reduced quantities: $\tau = \frac{T_c}{T}$, $\delta = \frac{\rho}{\rho_c}$
- Bank of terms for separate zero-density viscosity correlation:

$$\frac{\eta_{0,\mathrm{bank}}(T)}{\mu\mathrm{Pa\ s}} = \sum_{i=0}^{-8} A_{0,i}\tau^i \quad \mathrm{Result}: A_{0,-1} \text{ and } A_{0,-4}.$$

- Bank of terms for the total correlation:

$$\frac{\eta_{\mathrm{bank}}(T,\rho)}{\mu\mathrm{Pa\ s}} = \frac{\eta_0(T)}{\mu\mathrm{Pa\ s}}A_0 + \sum_{i=0}^{8}\sum_{j=1}^{20} A_{ij}\tau^i\delta^j + \sum_{k=0}^{5}\sum_{l=1}^{5} A_{kl}\tau^k\delta^l\,\mathrm{e}^{-\delta}$$
$$+ \sum_{m=0}^{1} A_m\tau\delta\mu_m\,\mathrm{e}^{-\beta_m(\delta-\gamma_m)^2-\varepsilon_m|\tau-\zeta_m|}.$$

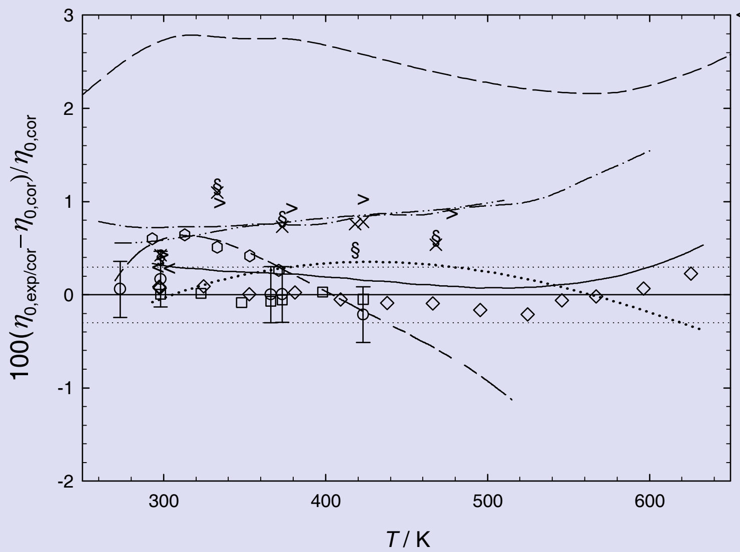
- Result for propane:

$$\frac{\eta_{\mathrm{cor},C_3H_8}(T,\rho)}{\mu\mathrm{Pa\ s}} = \sum_{i=1}^{12} A_i\tau^{t_i}\delta^{d_i} + A_{13}\tau^{t_{13}}\delta^{d_{13}}\,\mathrm{e}^{-\delta}$$
$$+ \sum_{i=14}^{15} A_i\tau\delta\,\mathrm{e}^{-\beta_i(\delta-1)^2-\varepsilon_i|\tau-1|}.$$

Comparison equation - experiment

Viscosity in the limit of zero density

- Agreement within the experimental uncertainty
- Error bars: ±0.3 %



◇, □, ○ experimental data in the limit of zero density

<, >, §, x experimental data at atmospheric pressure

⬡ secondary exp. data at atmospheric pressure

— — — Tanaka, Makita (1975)

— · · — Holland *et al.* (1979)

— — Tarzimanov *et al.* (1987)

— · — Younglove, Ely (1987)

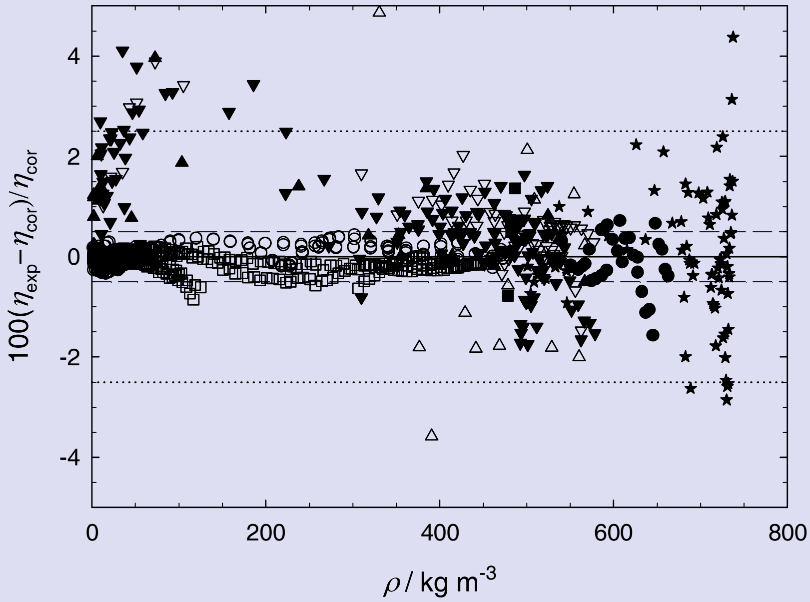
—— Vogel *et al.* (1998)

· · · Scalabrin *et al.* (2006)

Comparison equation - experiment

Viscosity in the fluid region

- New and re-evaluated data dominant
- Large deviations at small and high densities for earlier primary data
- Deviations of data in the near critical region $< \pm 0.35\%$



▽, △, ▼, ▲,

★, ■, ● earlier experimental data

□ re-evaluated experimental data

○ new experimental data

Comparison equation - experiment

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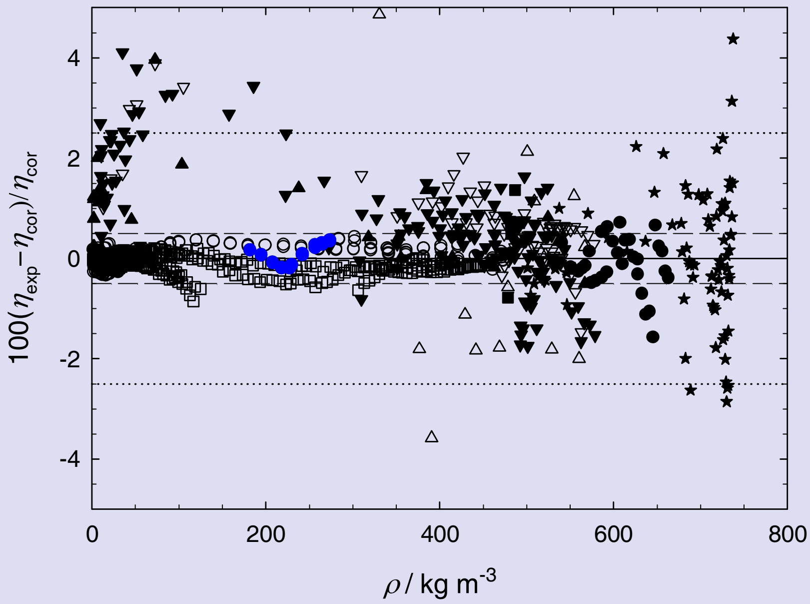


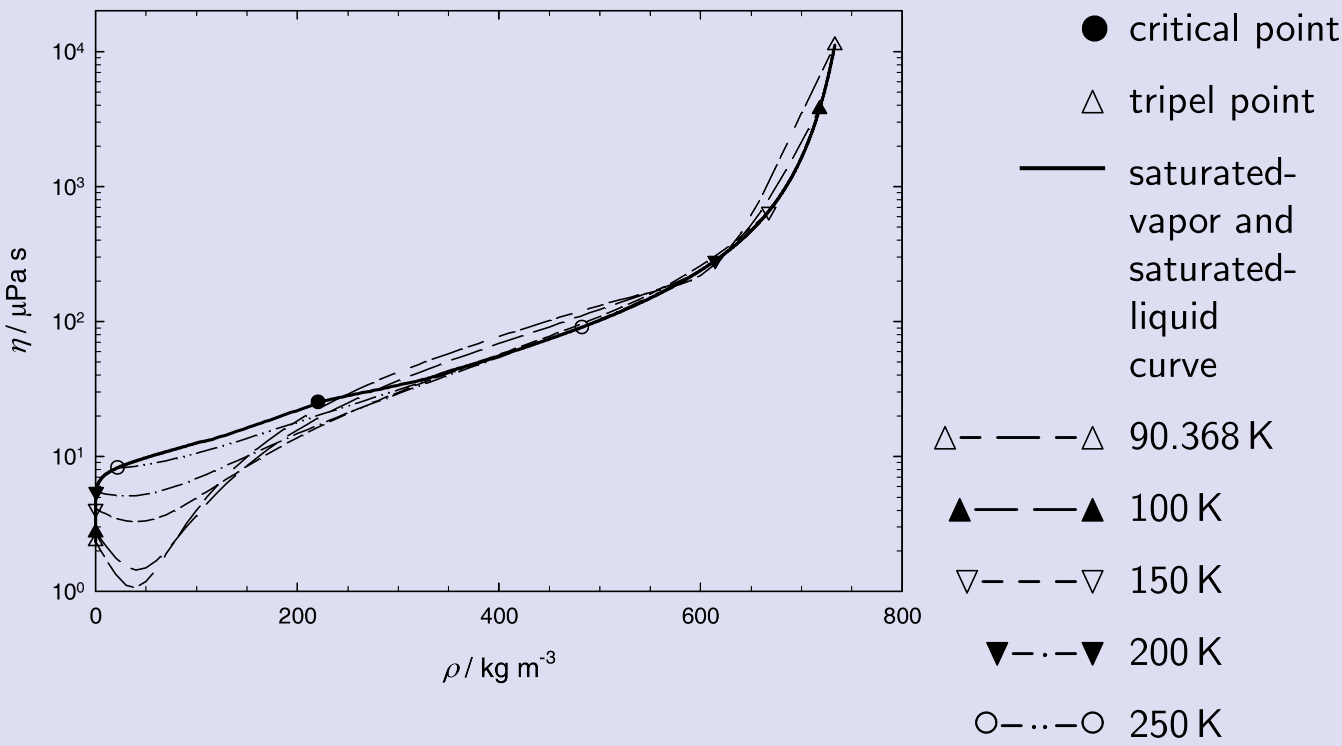
▽, △, ▼, ▲,

★, ■, ● earlier experimental data

□ re-evaluated experimental data

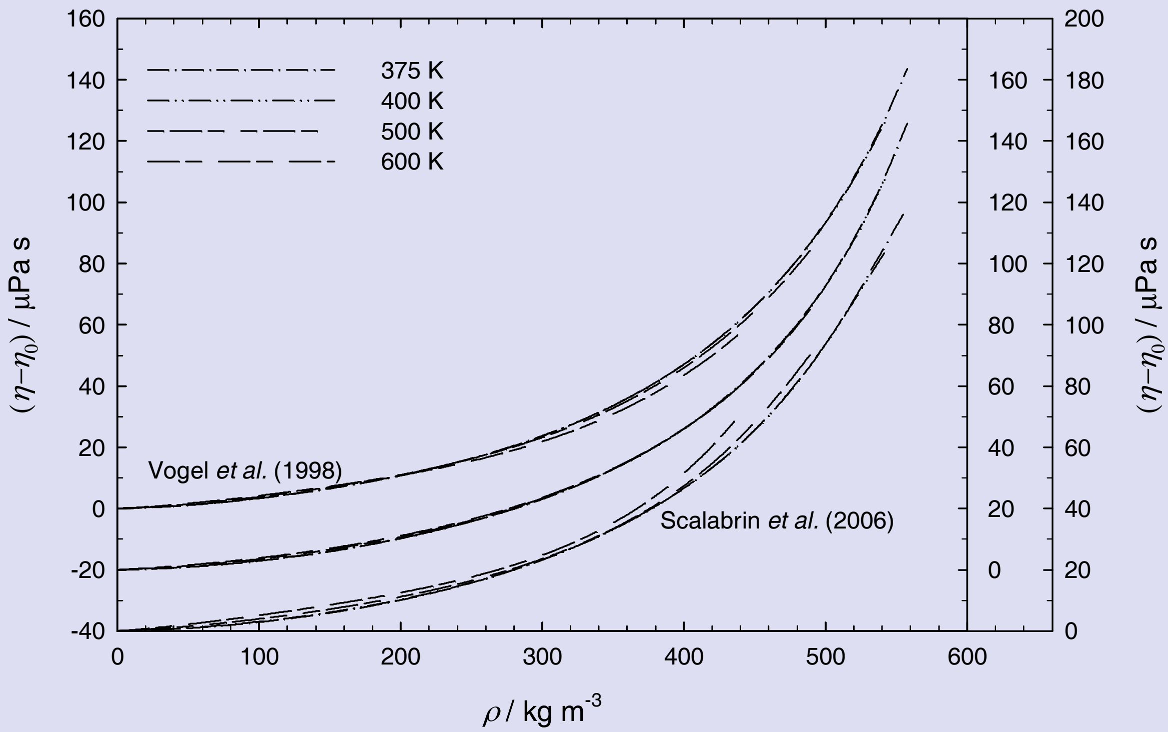
○ new experimental data

Propane – Correlation in the two-phase region



Propane – Consistency test using behavior of η_{Res}

Comparison to viscosity-surface correlations from literature: Vogel *et al.* (1998) and Scalabrin *et al.* (2006)



Conclusion and Outlook

- New viscosity-surface correlation was generated for propane based on new precise experimental viscosity data
- The structure-optimization method of Setzmann and Wagner (Ruhr-Universität Bochum) was used
- The viscosity was correlated as $\eta(T,\rho)$
- Critical enhancement was included using new data of Seibt *et al.*
  Theory: divergence at the critical point
  Correlation: finite values when approaching the critical point due to used experimental data from the near-critical region

- Further work on n-butane and isobutane

→ precise data using the vibrating-wire viscometer are available for these fluids

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S. Herrmann (Hochschule Zittau/Görlitz) Viscosity-Surface Correlation for Propane June 25th, 2015, S. 17