New Formulation for the Viscosity of Isobutane

Sebastian Herrmann[1], Hans-Joachim Kretzschmar[1], Eckhard Vogel[2]

[1]Hochschule Zittau/Görlitz – University of Applied Sciences,
Fachgebiet Technische Thermodynamik, Zittau, Germany

[2]Universität Rostock, Institut für Chemie, Rostock, Germany

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Outline

Motivation – Problems with Consistency

Isobutane: EOS, η, λ – inconsistent

- Correlations recommended in REFPROP[1]
  - EOS Bücker and Wagner (2006)[2]
  - η Vogel *et al.* (2000)[3]
  - λ Perkins (2002)[4]
- 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)[5], but again based on an old-fashioned classical MBWR

1 Lemmon, E. W., Huber, M. L., and McLinden, M. O., Standard Reference Data Program, National Institute of Standards and Technology, Gaithersburg (2013).
2 Bücker, D. and Wagner, W., *J. Phys. Chem. Ref. Data* **35**, 929-1019 (2006).
3 Vogel, E., Küchenmeister, C., Bich, E., *Int. J. Thermophys.*, **21**, 343-356 (2000).
4 Perkins, R. A., *J. Chem. Eng. Data*, **47**, 1272-1279 (2002).
5 Olchowy, G. A. and Sengers, J. V., *Phys. Rev. Lett.*, **61**, 15-18 (1988).

Isobutane – Correlation method using structure optimization

Selection criteria

- Combination of different terms
- Requirement of reliable experimental data
- Use of simple functional dependencies, e.g., $\eta = \eta(T, \rho)$

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

Isobutane — Primary experimental viscosity data

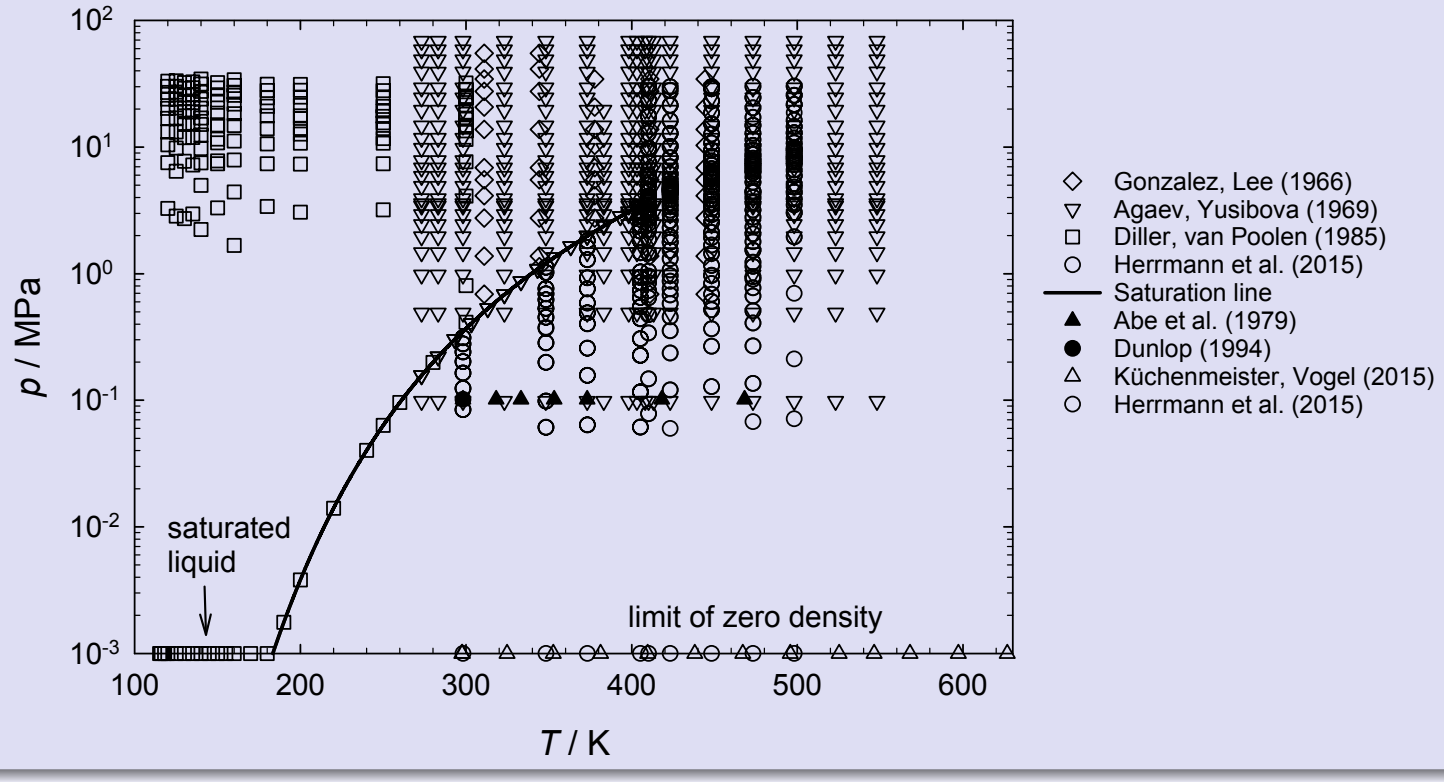
Authors	Year	Method[6]	Number of points	T K	ρ kg m^{-3}	$\Delta\eta/\eta$ %
Küchenmeister and Vogel	2015[7]	OD	14	298–627	0	0.3
Herrmann *et al.*	2015	VW	9	298–498	0	0.3
Abe *et al.*	1979	OD	7[8]	298–468	1.5–2.4	0.4–1.0
Dunlop	1994	C	1[8]	298	2.4	0.5
Gonzalez and Lee	1966	C	47	311–444	11–608	2.5
Agaev and Yusibova	1969	C	452	273–548	1.3–645	4.0
Diller and van Poolen	1985	OQC	141	115–300	548–748	2.5
Herrmann *et al.*	2015	VW	567	298–498	1.0–497	0.5

6 C, capillary; OD, oscillating disk; OQC, oscillating quartz crystal; VW, vibrating wire

7 re-evaluated data

8 Data virtually not used for developing the new viscosity formulation.

Isobutane — p,T diagram with primary experimental data



Isobutane — Terms for zero-density viscosity and initial density dependence

- Parts for zero-density viscosity and initial density dependence treated separately
- Using reduced quantities: $\tau = \frac{T_c}{T}$, $\delta = \frac{\rho}{\rho_c}$
- Bank of terms for separate zero-density viscosity correlation:

$$\eta_{0,\mathrm{bank}}(\tau) = \frac{A_{0,\mathrm{PF}}}{\tau^{1/2}\langle\sum_{j=-2}^{2}\sum_{i=0}^{3} A_{0,ij}(T_c/\tau)^{j/2}\{\exp\left[(T_c/\tau)^{1/3}\right]\}^{-i}\rangle}. \quad \text{Result}: A_{0,00}, A_{0,0-1}, A_{0,10}.$$

→ Extrapolation of $\eta_0(\tau)$ down to 0 K and up to 10000 K very reasonable

Motivation Method, Theory, and Results Comparisons Conclusion and Outlook

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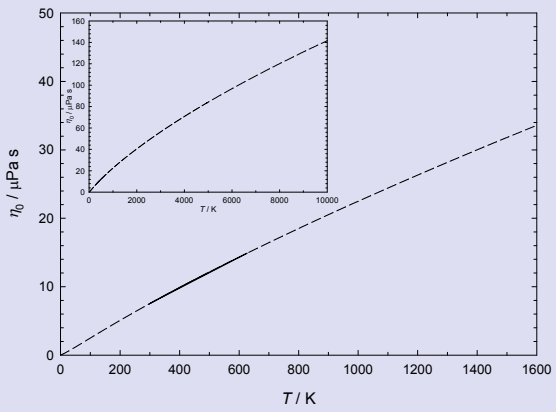

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Isobutane — Terms for zero-density viscosity and initial density dependence

- Rainwater-Friend theory[9,10] used for separate initial-density dependence of viscosity:

$$\eta_1(\tau) = \eta_0(\tau) A_{1,\mathrm{PF}} \left[\sum_{k=0}^{6} A_{1,k} (\tau)^{0.25k} + A_{1,7} \tau^{2.5} + A_{1,8} \tau^{5.5} \right] .$$

- Experimental data for B_η^* and η_1 of Küchenmeister and Vogel and of Herrmann *et al.* used to determine ε/k_B and σ needed for calculating coefficients $A_{1,k}$

9 Friend, D. G. and Rainwater, J. C., *Chem. Phys. Lett.* **107**, 590-594 (1984).
10 Rainwater, J. C. and Friend, D. G., *Phys. Rev. A* **36**, 4062-4066 (1987).

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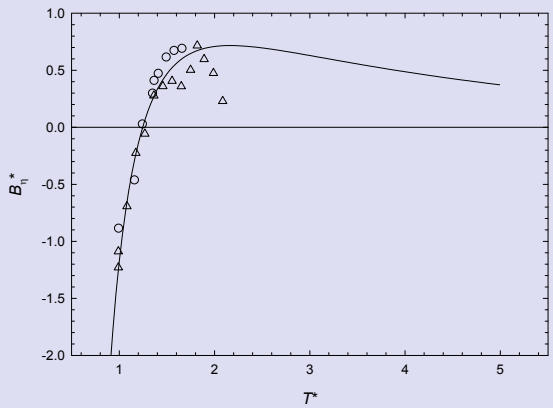

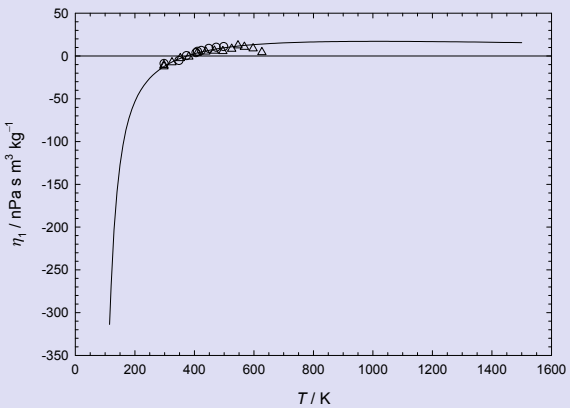

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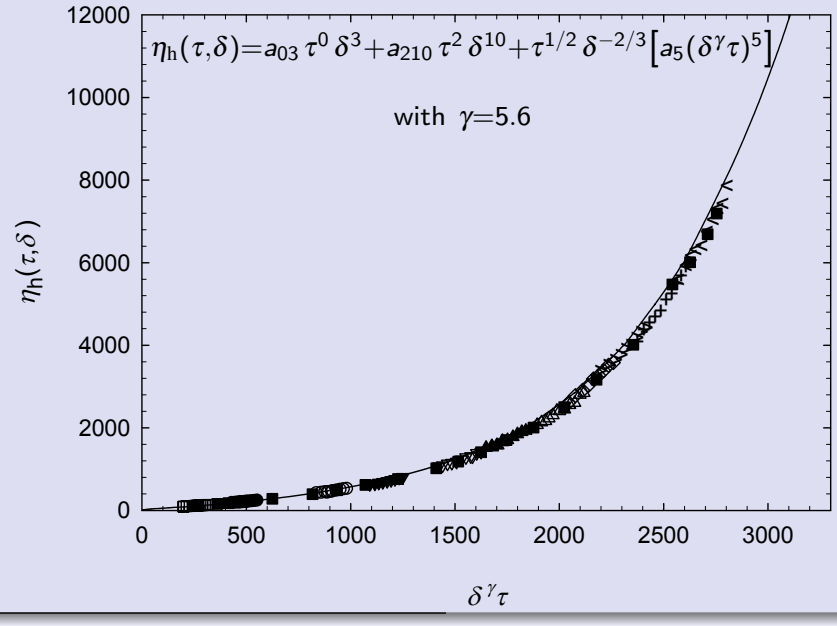
Isobutane — Thermodynamic scaling

- Viscosity represented by a single variable ρ^γ/T instead of separate variables ρ and T
- Scaling exponent γ separately be determined
- δ, τ used for higher density terms as unknown function $G(\delta^\gamma\tau)$, applied to exp. data[11]



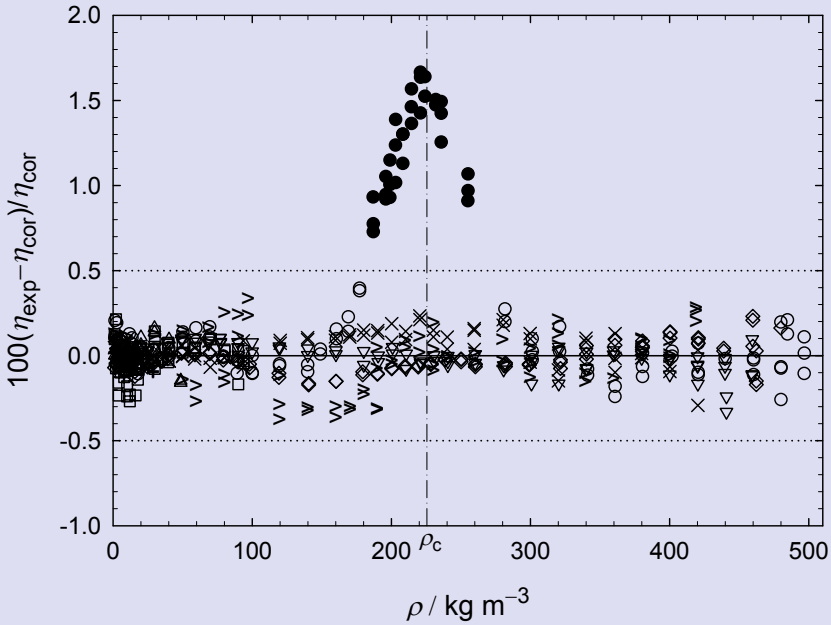
< 120 K
\+ 125 K
> 130 K
◇ 135 K
△ 140 K
▲ 150 K
▽ 160 K
▼ 180 K
○ 200 K
● 250 K
□ 300 K
■ saturated liquid
—— calculated values

[11] Diller, D. E. and van Poolen, L. J., *Int. J. Thermophys.* **6**, 43-62 (1985).

Isobutane — Critical enhancement of viscosity

New data for isobutane of Herrmann *et al.* (2015)[12] compared to preliminary correlation

- Deviations up to +1.67 % near critical density ($\rho_c = 225.5$ kg m^{-3})



< 298.15 K
\+ 348.15 K
△ 373.15 K
□ 405.15 K
○ 410.15 K
◇ 423.15 K
▽ 448.15 K
X 473.15 K
> 498.15 K
● 410.15 K, data influenced by critical enhancement

[12] Herrmann, S., Hassel, E., and Vogel, E., *AIChE J.*, **61**, 3116-3137 (2015).

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).

Viscosity-surface correlation for Isobutane

Bank of terms for higher-density and critical regions

- Reduced quantities: $\tau = \frac{T_c}{T}$, $\delta = \frac{\rho}{\rho_c}$
- Bank of terms for the higher-density terms and the critical region:

$$\eta - \eta_0(\tau) - \eta_1(\tau)\delta = \eta_{h+c,bank}(\tau,\delta) = \sum_{i=0}^{5}\sum_{j=2}^{10} A_{ij}\tau^i\delta^j + \tau^{1/2}\delta^{-2/3}\left[\sum_{k=1}^{5} A_k(\delta^\gamma\tau)^k\right] + \sum_{m=0}^{1} A_m\tau\delta\mu_m \mathrm{e}^{-\beta_m(\delta-\gamma_m)^2-\varepsilon_m|\tau-\zeta_m|}.$$

Viscosity-surface correlation for Isobutane

Final result for viscosity of isobutane

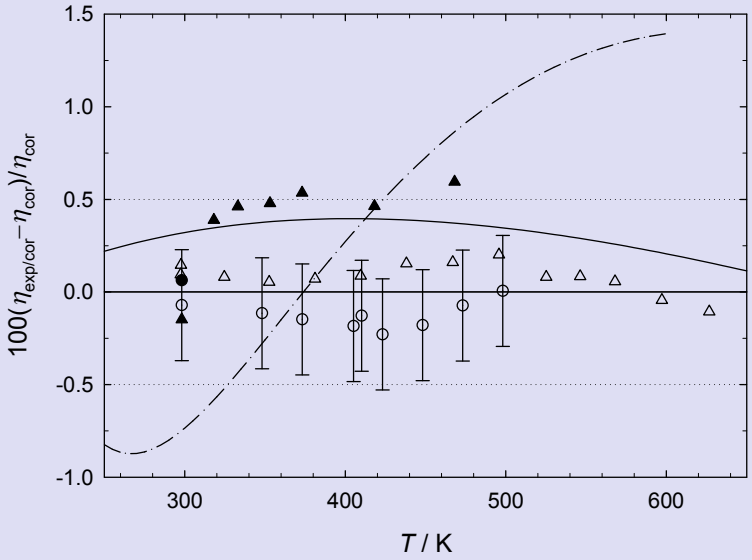
- Reduced quantities: $\tau = \frac{T_c}{T}$, $\delta = \frac{\rho}{\rho_c}$
- Separate zero-density viscosity and initial-density dependence correlation
- Result from structure-optimization method for higher-density and critical regions

$$\begin{aligned}\eta_{\mathrm{cor,i-C_4H_{10}}}(\tau,\delta) &= \frac{A_{0,\mathrm{PF}}}{\tau^{1/2}\left[A_{0,0}\tau^{1/2}(T_c)^{-1/2} + A_{1,0} + A_{2,0}\,\mathrm{e}^{-(T_c/\tau)^{1/3}}\right]} \\ &\times \left\{1 + A_{1,\mathrm{PF}}\left[\sum_{k=0}^{6} A_{1,k}(\tau)^{0.25k} + A_{1,7}\tau^{2.5} + A_{1,8}\tau^{5.5}\right]\delta\right\} \\ &+ \sum_{i=1}^{10} A_i \tau^{t_i}\delta^{d_i} + \tau^{1/2}\delta^{-2/3}A_{11}(\delta^{5.6}\tau)^4 \\ &+ \sum_{i=12}^{13} A_i \tau\delta\,\mathrm{e}^{-\beta_i(\delta-1)^2-\varepsilon_i|\tau-1|}.\end{aligned}$$

Comparison equation vs. experiment and correlations

Viscosity in the limit of zero density and at low densities

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



△, ○ experimental data in the limit of zero density

▲, ● experimental data at atmospheric pressure

– · – correlation by Younglove and Ely (1987)[14]

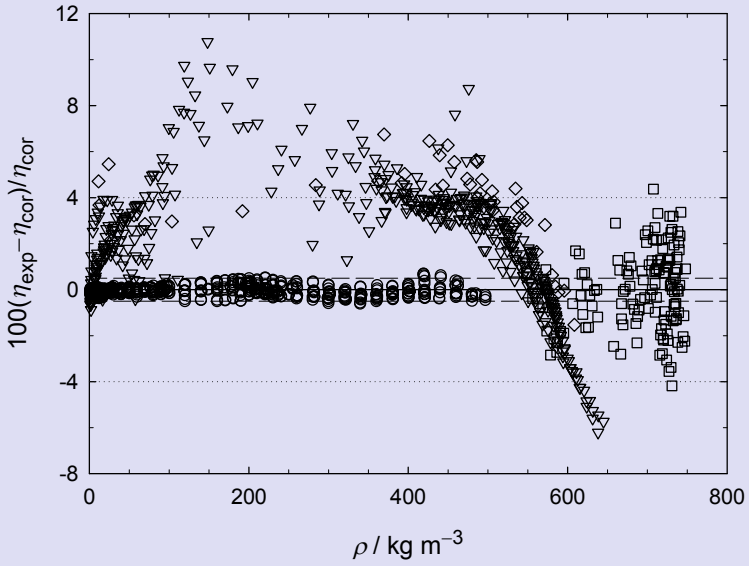
—— correlation by Vogel *et al.* (2000)

[14] Younglove, B. A. and Ely, J. F., *J. Phys. Chem. Ref. Data* **16**, 577-798 (1987).

Comparison equation vs. experiment

Viscosity in the fluid region

- New data dominant
- Large deviations particularly at small and high densities for earlier primary data



▽,◇,□ earlier experimental data

○ new experimental data

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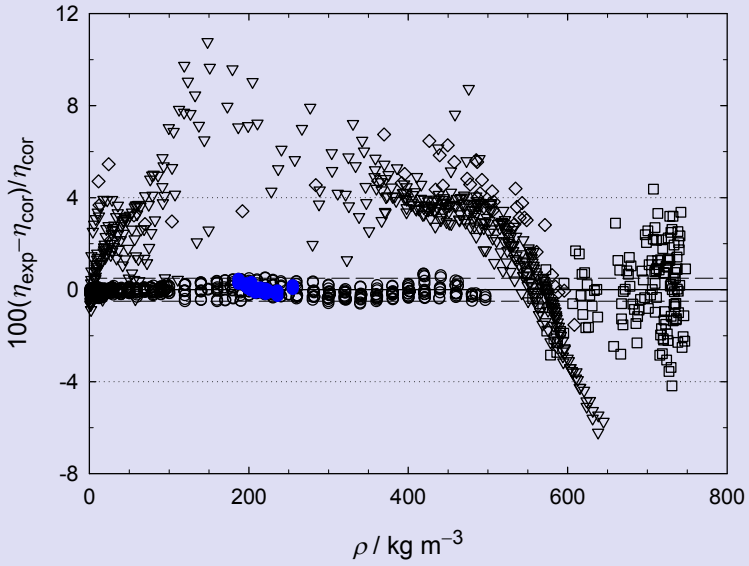

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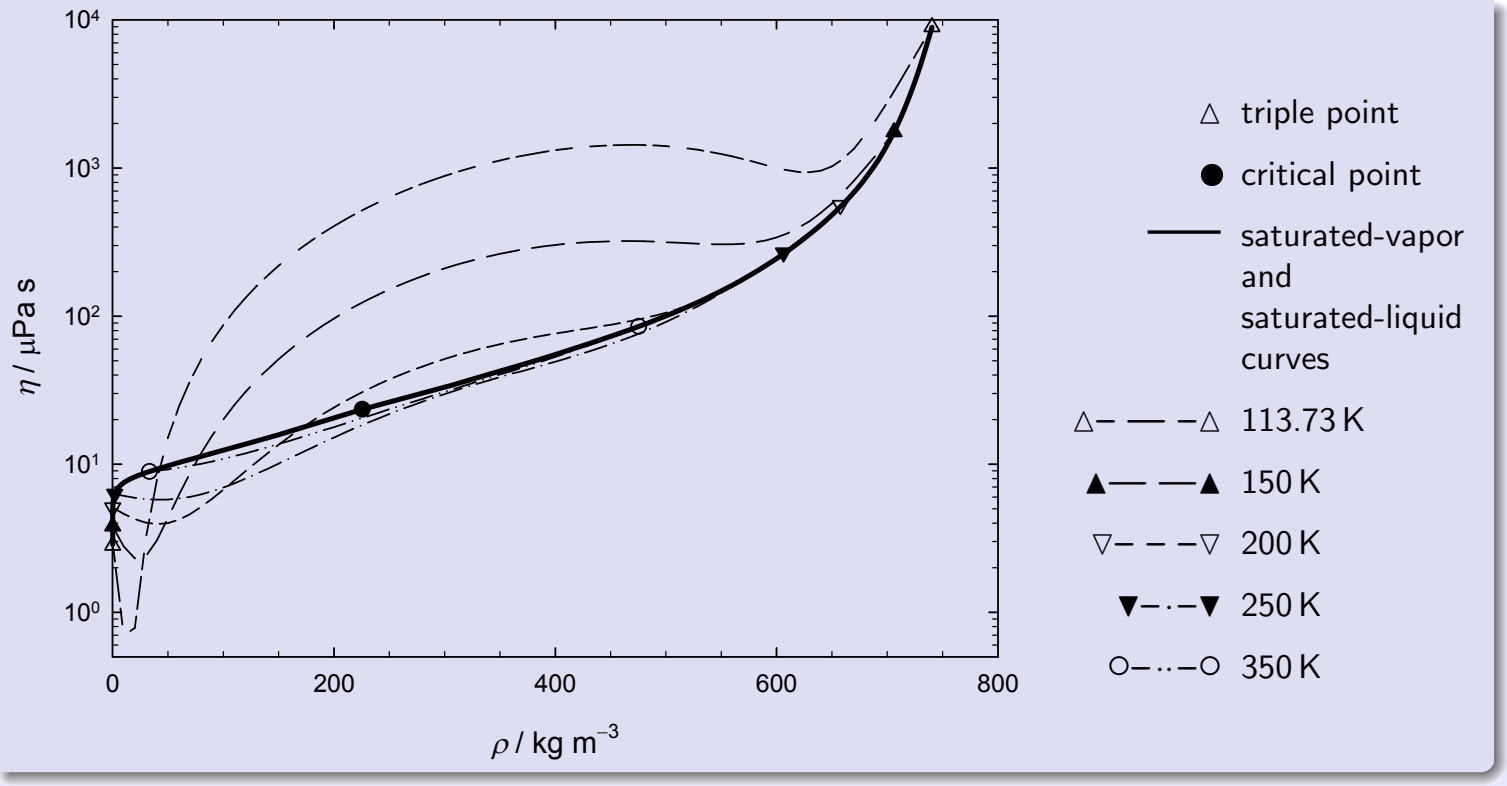
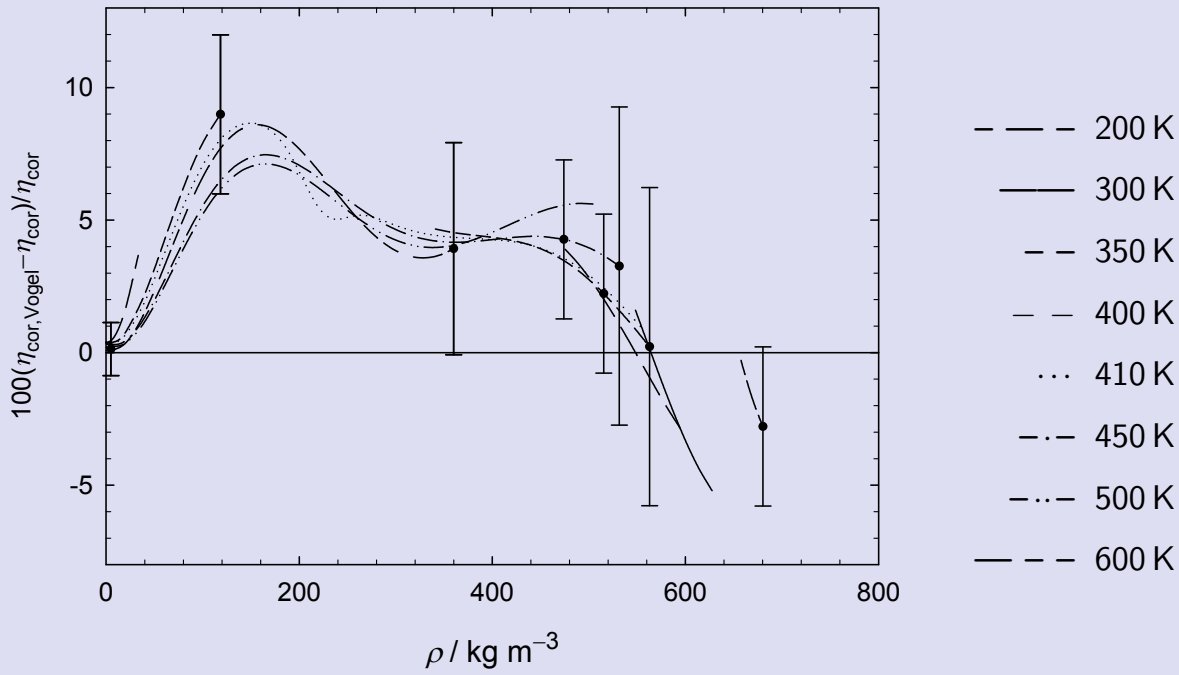
Behavior in the two-phase region



Comparison to viscosity formulation from literature

Viscosity formulation of Vogel *et al.* (2000)

- Error bars: uncertainty of former correlation of Vogel *et al.*



Conclusion and Outlook

- New viscosity formulation was generated for isobutane 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 $\eta(\tau, \delta)$
- The zero-density and initial-density viscosity parts were treated separately
- Thermodynamic scaling for higher-density terms, scaling exponent γ inferred
- Critical enhancement was included using new data of Herrmann *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

- Investigation on further fluids for which new experimental data are available in literature

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