Development of Viscosity Formulations for Working Fluids Using a Structure-Optimization Method

Sebastian Herrmann[1], Hans-Joachim Kretzschmar[1], Eckhard Vogel[2], Karsten Meier[3]

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

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

[3]Helmut-Schmidt-Universität/Universität der Bundeswehr Hamburg, Institut für Thermodynamik, Hamburg, Germany

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Outline

Motivation – Problems with Consistency

Example isobutane: EOS inconsistent with η

- Correlations recommended in REFPROP[1]:
  - EOS Bücker and Wagner (2006)[2]
  - η Vogel *et al.* (2000)[3]
- Model type
  - EOS classical including the critical region, an additional parametric crossover EOS not needed
  - η classical, but not including a critical enhancement, primary data conversion $\rho(p,T)$ based on an old-fashioned classical MBWR EOS (Younglove and Ely, 1987)[4]

Example water: EOS consistent with η

1 Lemmon, E. W., Bell, I. H., Huber, M. L., and McLinden, M. O., Standard Reference Data Program, National Institute of Standards and Technology, Boulder (2018).
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 Younglove, B. A. and Ely, J. F., *J. Phys. Chem. Ref. Data* **16**, 577-798 (1987).

Motivation – Problems in Near-Critical Region

Example water: η_c – calculation suitable for engineering use, but complicated equations

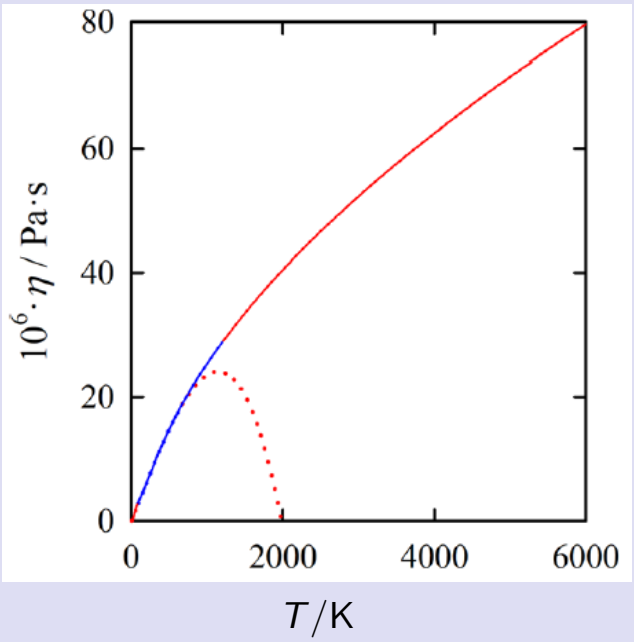
- Viscosity η of water (Huber *et al.*, 2009[5]):
  viscosity in near-critical region modelled by closed-form solution of Bhattacharjee *et al.* (1981)[6]
- Calculation speed in process simulations low due to complicated algorithms

Example isobutane: no critical enhancement included

5 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).
6 Bhattacharjee, J. K., Ferrell, R. A., Basu, R. S., and Sengers, J. V., *Phys. Rev. A* **24**, 1469-1475 (1981).

Motivation – Problems with Extrapolation Behaviour

Example ethane: η_0 correlation of Vogel *et al.* (2015)[7] replaced by that of Hellmann (2018)[8]



Values of Vogel *et al.* (2015)
Values of Hellmann (2018) in the range of validity
Values of Hellmann (2018), extrapolated

(Figure taken from Ref. 8)

7 Vogel, E., Span, R., Herrmann, S., *J. Phys. Chem. Ref. Data* **44**, 043101 (2015).
8 Hellmann, R., *J. Chem. Eng. Data* **63**, 470-481 (2018).

Correlation Method Employing Structure Optimization

Selection criteria

- Development of functional form from a larger bank of terms
- Requirement of reliable experimental data
- Use of theoretically based functional dependencies, e.g., $\eta = \eta(T, \rho)$

Procedure

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

Residual-quantity concept

- Viscosity correlation consists of different additive contributions

$$\eta = \eta_0(\tau) + \underbrace{\eta_1(\tau)\delta + \eta_h(\tau,\delta)}_{\eta_{res}(\tau,\delta)} + \eta_c(\tau,\delta) \quad \text{with} \quad \tau = \frac{T_c}{T}, \delta = \frac{\rho}{\rho_c}.$$

Zero-Density Viscosity and Initial Density Dependence

- Contributions for zero-density viscosity and initial density dependence treated separately
- Reduced quantities used: $\tau = \frac{T_c}{T}$, $\delta = \frac{\rho}{\rho_c}$
- Bank of terms for separate zero-density viscosity correlation (e.g. isobutane):

$$\eta_{0,\mathrm{bank}}(\tau) = \frac{A_{0,\mathrm{PF}}}{\tau^{1/2}\left\langle \sum_{j=-2}^{2}\sum_{i=0}^{3} A_{0,ij}\,(T_c/\tau)^{j/2}\left\{\exp\left[(T_c/\tau)^{1/3}\right]\right\}^{-i}\right\rangle}.$$ Result : 3 out of 20 terms.

→ Extrapolation of $\eta_0(\tau)$ down to 0 K and up to 10 000 K very reasonable

Motivation Method, Theory, and Fitting Procedure Results Conclusion and Outlook

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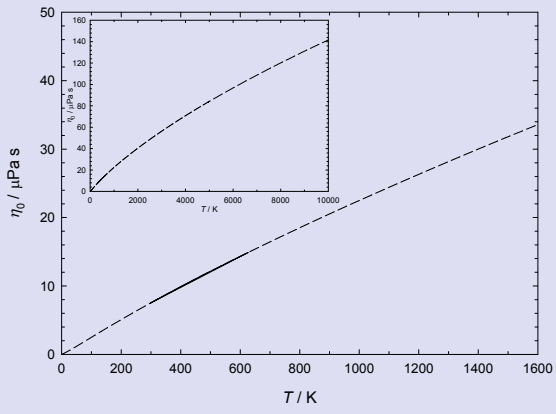

——— Temperature range of experimental data

— — Extrapolated temperature range

Zero-Density Viscosity and Initial Density Dependence

- Rainwater-Friend theory[9,10] with correlation for second viscosity virial coefficient B_η by Vogel *et al.* (1998)[11] used for separate initial-density dependence of viscosity:

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

- E.g. isobutane: experimental data for B_η^* and η_1 of Küchenmeister and Vogel[12] and of Herrmann *et al.*[13] 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).
11 Vogel, E., Küchenmeister, C., Bich, E., and Laesecke, A., *J. Phys. Chem. Ref. Data*, **27**, 947-970 (1998).
12 Herrmann, S. and Vogel, E., *J. Phys. Chem. Ref. Data* (2018), to be submitted.
13 Herrmann, S., Hassel, E., and Vogel, E., *AIChE J.*, **61**, 3116-3137 (2015).

Motivation Method, Theory, and Fitting Procedure Results Conclusion and Outlook

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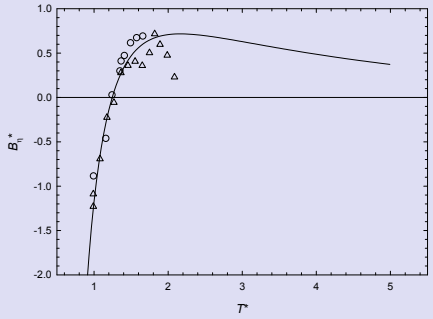

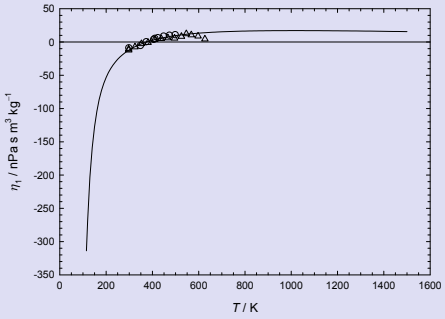

Calculated values
△ Küchenmeister and Vogel (re-evaluated, 2018)
○ Herrmann *et al.* (2015)

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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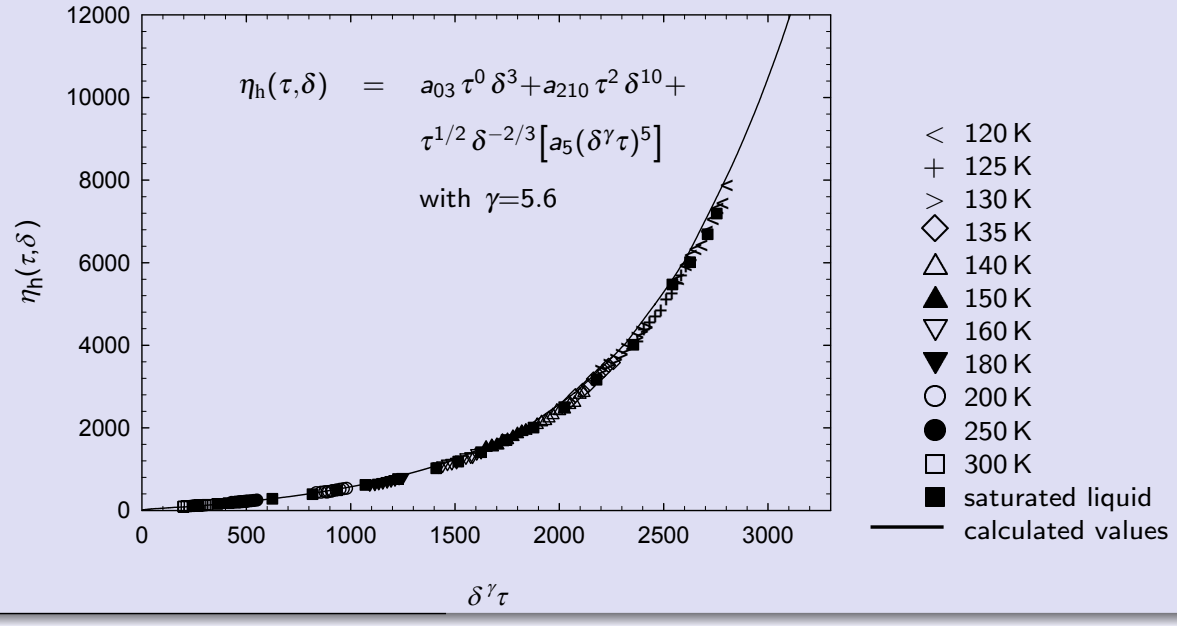
S. Herrmann (Hochschule Zittau/Görlitz) Development of Viscosity Formulations September 5th, 2018, S. 8

Thermodynamic Scaling for High-Dense Region

- Viscosity represented by a single variable ρ^γ/T instead of separate variables ρ and T
- Scaling exponent γ separately determined, e.g., isobutane: $\gamma = 5.6$
- δ, τ used for higher density terms as unknown function $G(\delta^\gamma\tau)$, applied to exp. data[14]

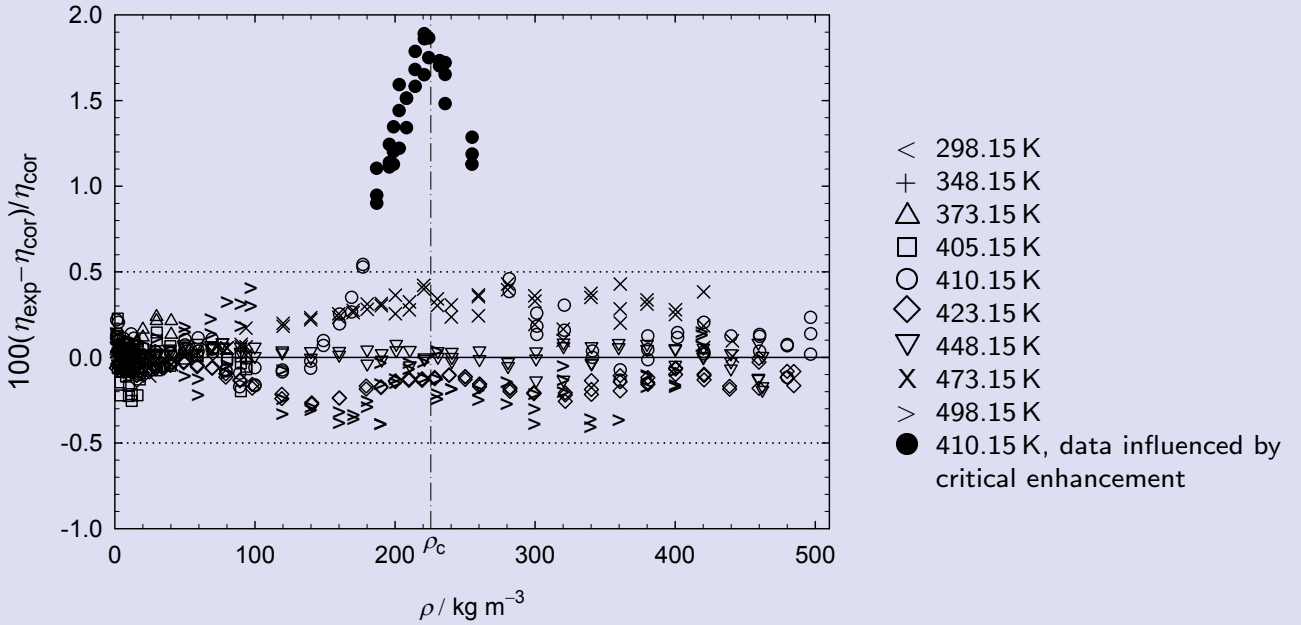


[14] Diller, D. E. and van Poolen, L. J., *Int. J. Thermophys.* **6**, 43-62 (1985).

Critical Enhancement of Viscosity

Experimental data partly influenced by critical enhancement

- New data of Herrmann *et al.* (2015) for isobutane show deviations up to +1.9 % near critical density ($\rho_c = 225.5$ kg m^{-3}) from preliminary correlation



Critical Enhancement of Viscosity

Theory according to Bhattacharjee *et al.* (1981)[15]

- Viscosity η is modelled as an asymptotic power-law divergence:

$$\eta \approx \eta_b (Q_0 \xi)^{z_\eta} \quad \text{with} \quad \eta_b = \eta_0 + \eta_{res}.$$

- Critical enhancement represents a multiplicative anomaly:

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

- Crossover is needed $\longrightarrow$ used within the mode-coupling theory, simplified closed-form solution developed by Bhattacharjee *et al.* (1981) $\longrightarrow$ recently used in IAPWS formulation for the viscosity of water (Huber *et al.*, 2009[16]):

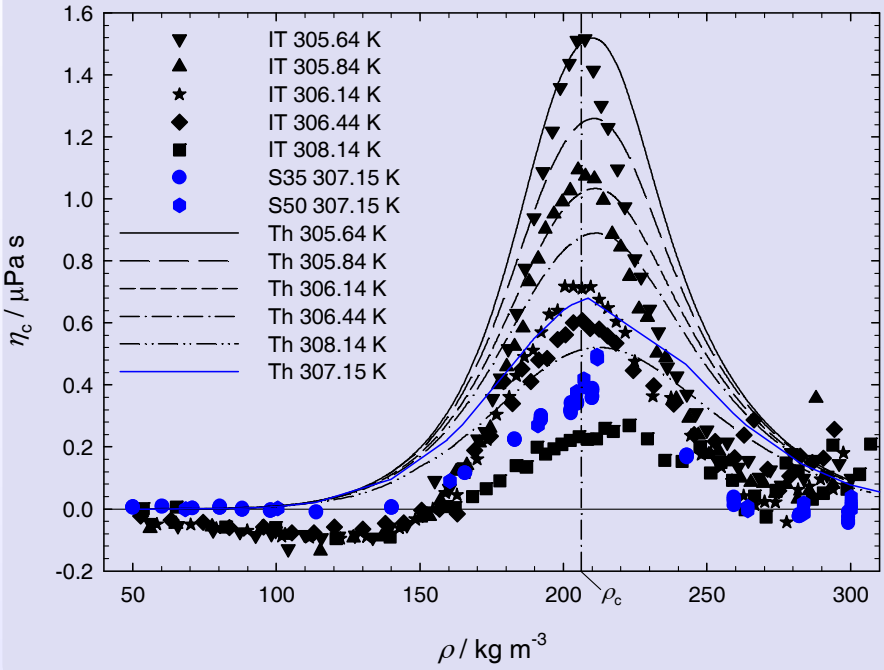
$$\eta_c = \eta_b [\exp(z_\eta Y) - 1] \ .$$

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

16 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).

Critical Enhancement of Viscosity

Ethane: theory vs. experiment



- Theory: divergence at the critical point
- Solution by Bhattacharjee *et al.*: finite values for viscosity when approaching the critical point

→ Suitable for engineering use

→ Development of terms feasible for use with structure-optimization method

→ Terms adjusted employing experimental data

T_c: 305.322 K

IT Iwasaki and Takahashi (1981)[17]

S35 Seibt *et al.* (2011)[18], purity grade of sample: 3.5

S50 Seibt *et al.* (2011), purity grade of sample: 5.0

Th lines show calculated values using Bhattacharjee *et al.* (1981)

17 Iwasaki, H. and Takahashi, M., *J. Chem. Phys.* **74**, 1930-1943 (1981).

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

Example Isobutane – Viscosity Correlation

Residual-quantity concept

- Viscosity correlation consists of different additive contributions

$$\eta = \eta_0(\tau) + \eta_1(\tau)\delta + \eta_h(\tau,\delta) + \eta_c(\tau,\delta).$$

Bank of terms for high-density and near-critical regions

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

$$\begin{aligned}\eta_h(\tau,\delta) + \eta_c(\tau,\delta) &= \sum_{i=0}^{5}\sum_{j=2}^{10} A_{ij}\tau^i\delta^j + \tau^{1/2}\delta^{-2/3}\left[\sum_{k=1}^{5} A_k(\delta^\gamma\tau)^k\right] && \leftarrow \eta_h \\ &\quad + \sum_{m=0}^{1} A_m\tau\delta\mu_m\, e^{-\beta_m(\delta-\gamma_m)^2-\varepsilon_m|\tau-\zeta_m|}. && \leftarrow \eta_c\end{aligned}$$

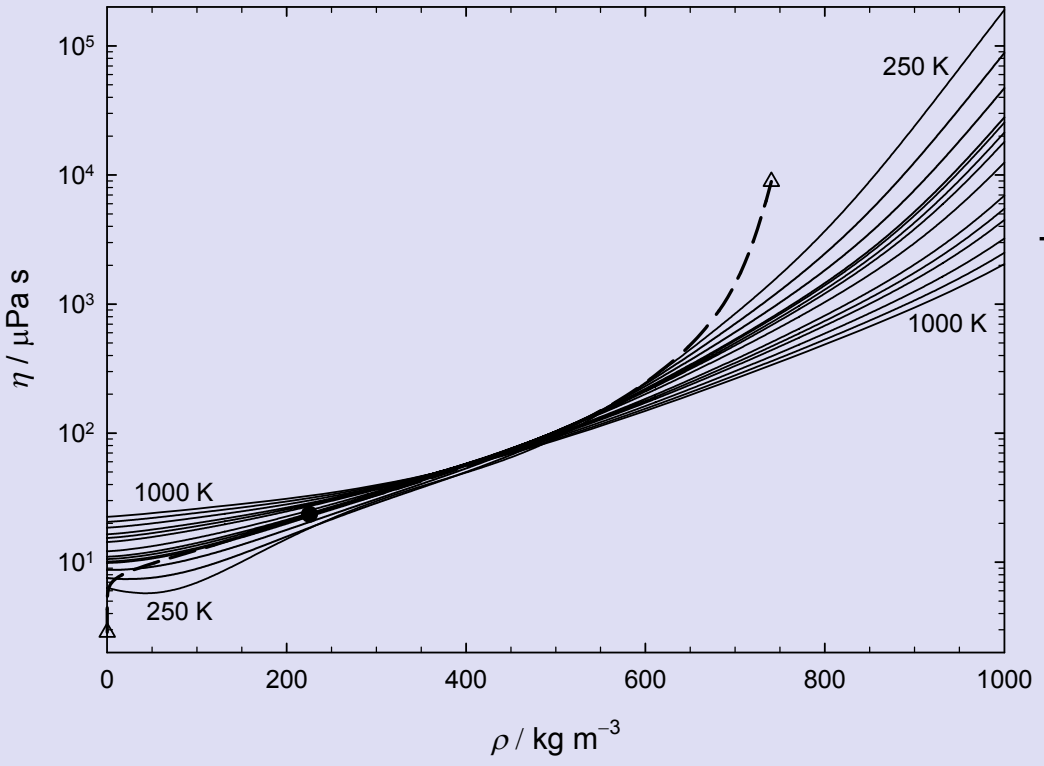
Example Isobutane – Viscosity Correlation

Final result for viscosity, e.g., isobutane

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

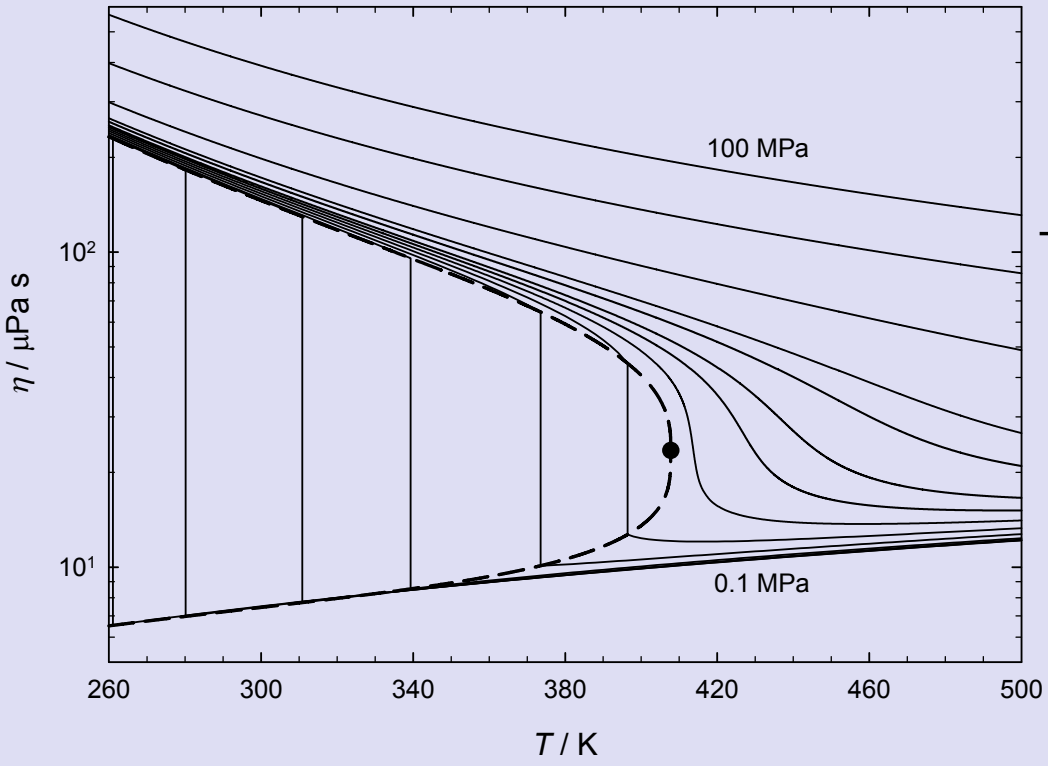
$$\begin{aligned}\eta_{cor}(\tau,\delta) &= \frac{A_{0,PF}}{\tau^{1/2}\left[A_{0,0}\tau^{1/2}(T_c)^{-1/2} + A_{1,0} + A_{2,0}\, e^{-(T_c/\tau)^{1/3}}\right]} \\ &\quad \times \left\{1 + A_{1,PF}\left[\sum_{k=0}^{6} A_{1,k}(\tau)^{0.25k} + A_{1,7}\tau^{2.5} + A_{1,8}\tau^{5.5}\right]\delta\right\} \\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

Example Isobutane – Viscosity Isotherms as Function of Density ρ



- ● Critical point
- △ Triple point
- — — saturated-vapor curve and saturated-liquid curve
- —— Isotherms at (250, 300, 350, 400, 410, 450, 500, 600, 650, 700, 800, 900, and 1000) K

Example Isobutane – Viscosity Isobars as Function of Temperature T

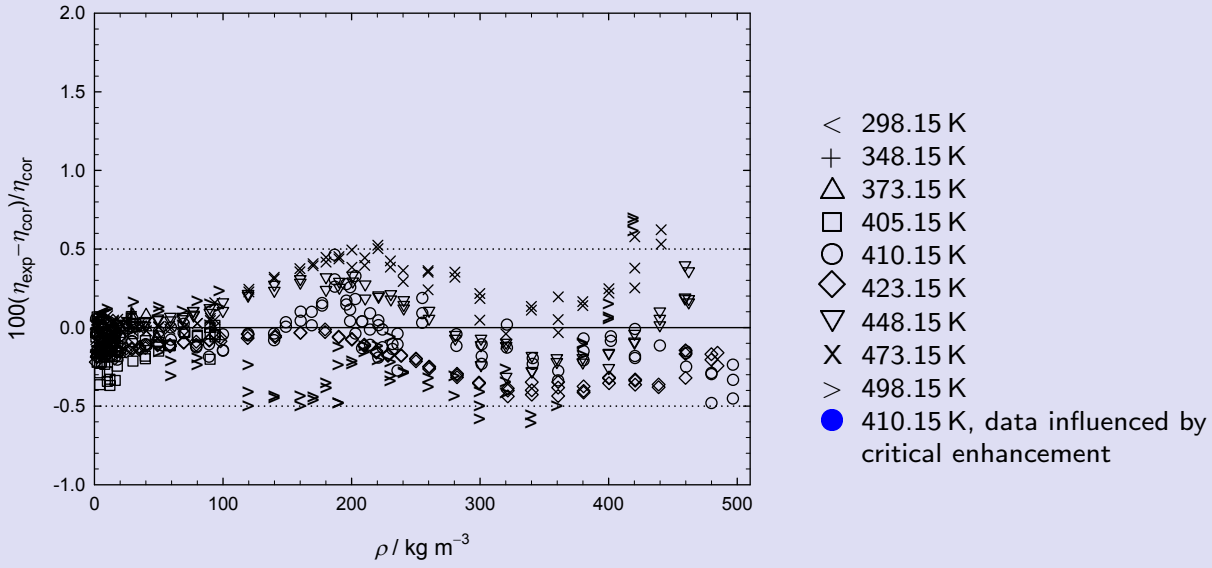


- ● Critical point
- — — saturated-vapor curve and saturated-liquid curve
- —— Isobars at (0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 8, 10, 20, 50, and 100) MPa

Example Isobutane – Comparison Equation vs. Experiment

Viscosity in the fluid and near-critical region

- New data of Herrmann *et al.* (2015) described within experimental uncertainty
- Deviations of data in the near-critical region $< \pm 0.34\%$, one outlier at 0.46%



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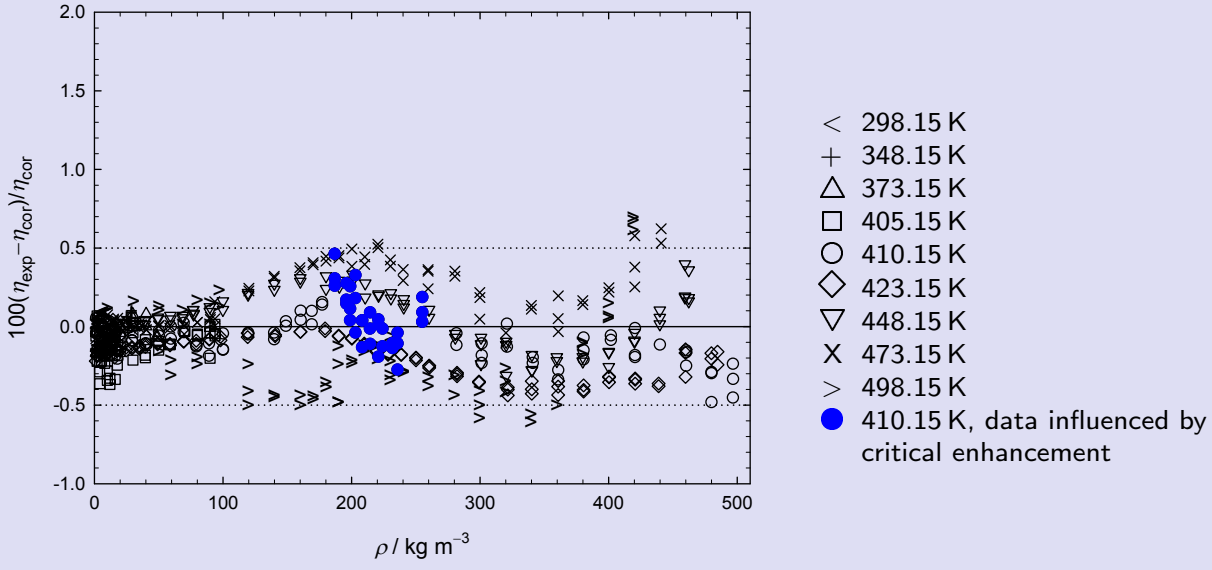

Conclusion and Outlook

Conclusion I

- The residual-quantity concept was applied to determine the functional form of the formulations
- 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 contributions were treated separately
- Thermodynamic scaling was used for high-density terms,
  scaling exponent γ inferred for isobutane
- New term format for critical enhancement of viscosity was developed
- The extrapolation behavior to low and high temperatures and pressures is reasonable

Conclusion and Outlook

Conclusion II

- New formulations describe all important thermodynamic regions with a simplified equation due to use of the structure-optimization method
- Recently developed viscosity correlations using structure-optimization method
  - Ethane: Vogel *et al.* (2015) and Herrmann *et al.* (Update 2018)
  - Propane: Vogel and Herrmann (2016)
  - *n*-Butane: Herrmann and Vogel (2018)
  - Isobutane: Herrmann and Vogel (to be submitted 2018)
- All correlations are implemented or subject to implement into REFPROP as reference formulations for viscosity of each fluid

Outlook

- Update for Propane in preparation (to be submitted to *J. Phys. Chem. Ref. Data*)
- Investigation on further fluids for which new experimental data will become available
  → cooperation with Prof. K. Meier, Helmut-Schmidt-Universität, Hamburg

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