

New Formulation for the Viscosity of Isobutane

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Outline

- 1 Motivation
- 2 Method, Theory, and Results
 - Structure-optimization method
 - Choice of primary data sets
 - Choice of terms for different fluid regions
 - New viscosity formulation
- 3 Comparisons
 - Viscosity in the limit of zero density and at low densities
 - Viscosity in the fluid region
- 4 Conclusion and Outlook

Motivation – Problems with Consistency

Isobutane: EOS, η , λ – inconsistent

- Correlations recommended in REFPROP¹

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 Olchoway 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 Olchoway, 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

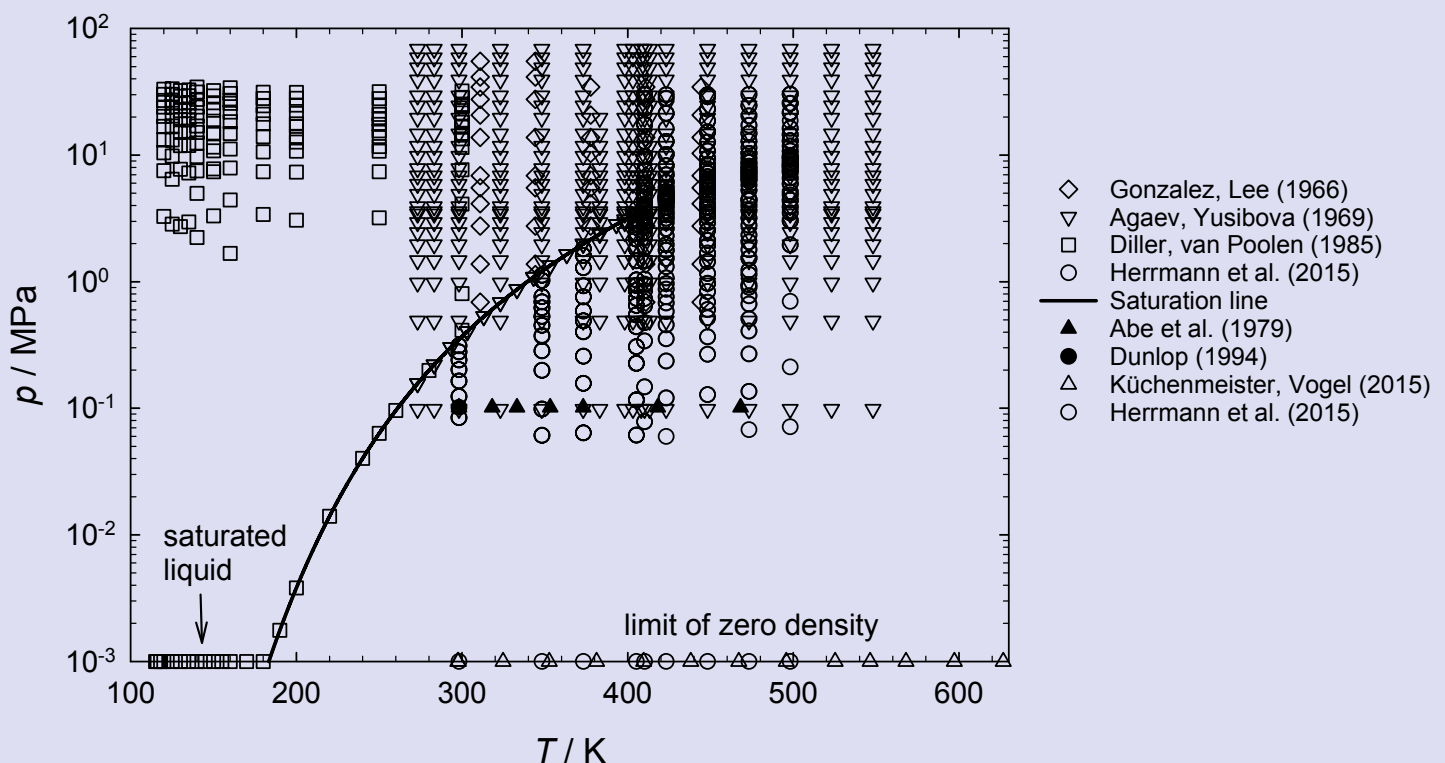
Authors	Year	Method ⁶	Number of points	T K	ρ kg m^{-3}	$\Delta\eta/\eta$ %
Küchenmeister and Vogel	2015 ⁷	OD	14	298–627	0	0.3
Herrmann <i>et al.</i>	2015	VW	9	298–498	0	0.3
Abe <i>et al.</i>	1979	OD	7 ⁸	298–468	1.5–2.4	0.4–1.0
Dunlop	1994	C	1 ⁸	298	2.4	0.5
Gonzalez and Lee	1966	C	47	311–444	11–608	2.5
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 <i>et al.</i>	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:

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

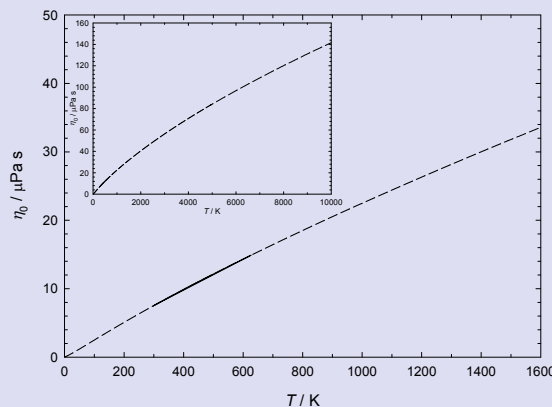
→ Extrapolation of $\eta_0(\tau)$ down to 0 K and up to 10000 K very reasonable

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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:

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

- 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).

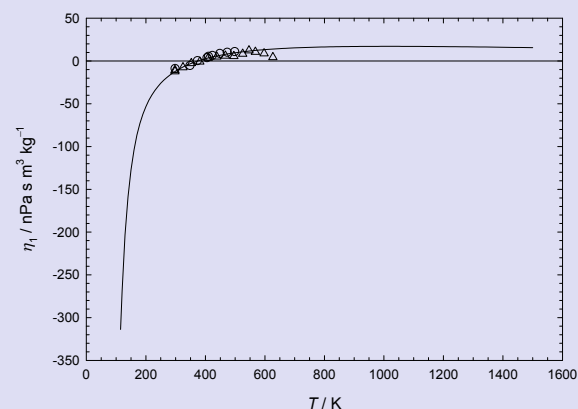
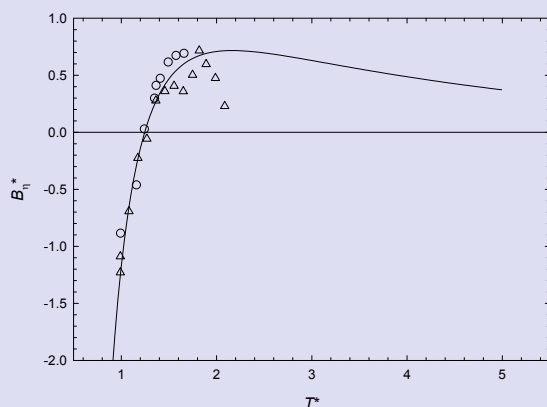
¹⁰ Rainwater, J. C. and Friend, D. G., *Phys. Rev. A* **36**, 4062-4066 (1987).

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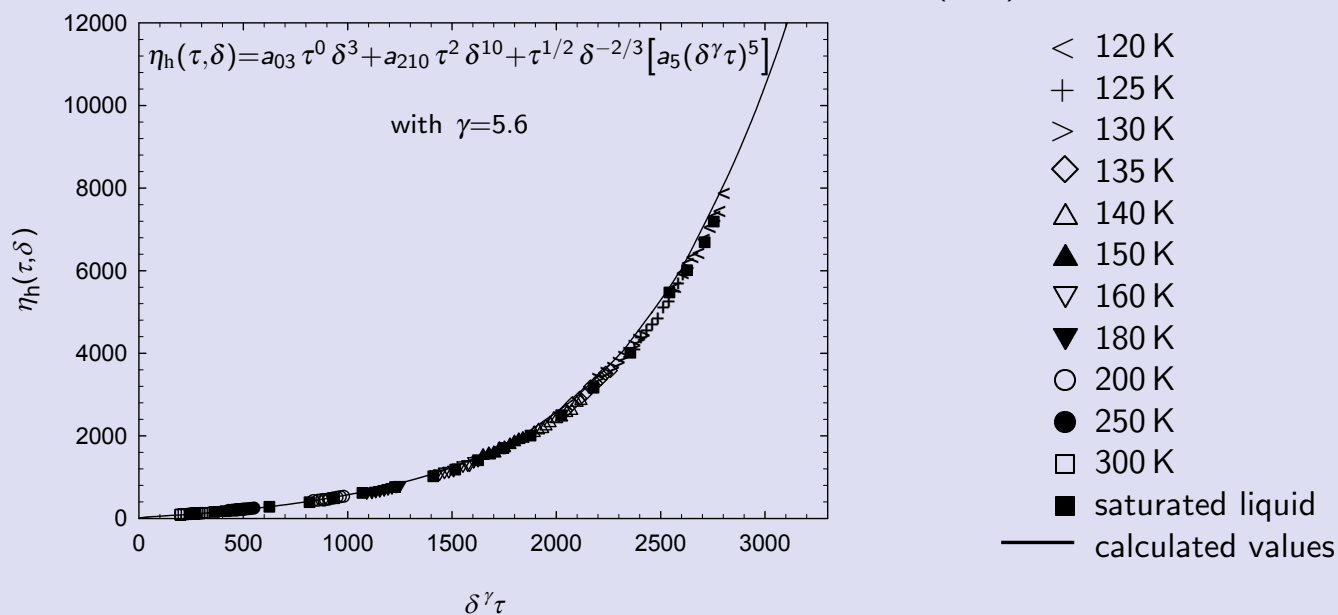


⁹ Friend, D. G. and Rainwater, J. C., *Chem. Phys. Lett.* **107**, 590-594 (1984).

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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. data¹¹

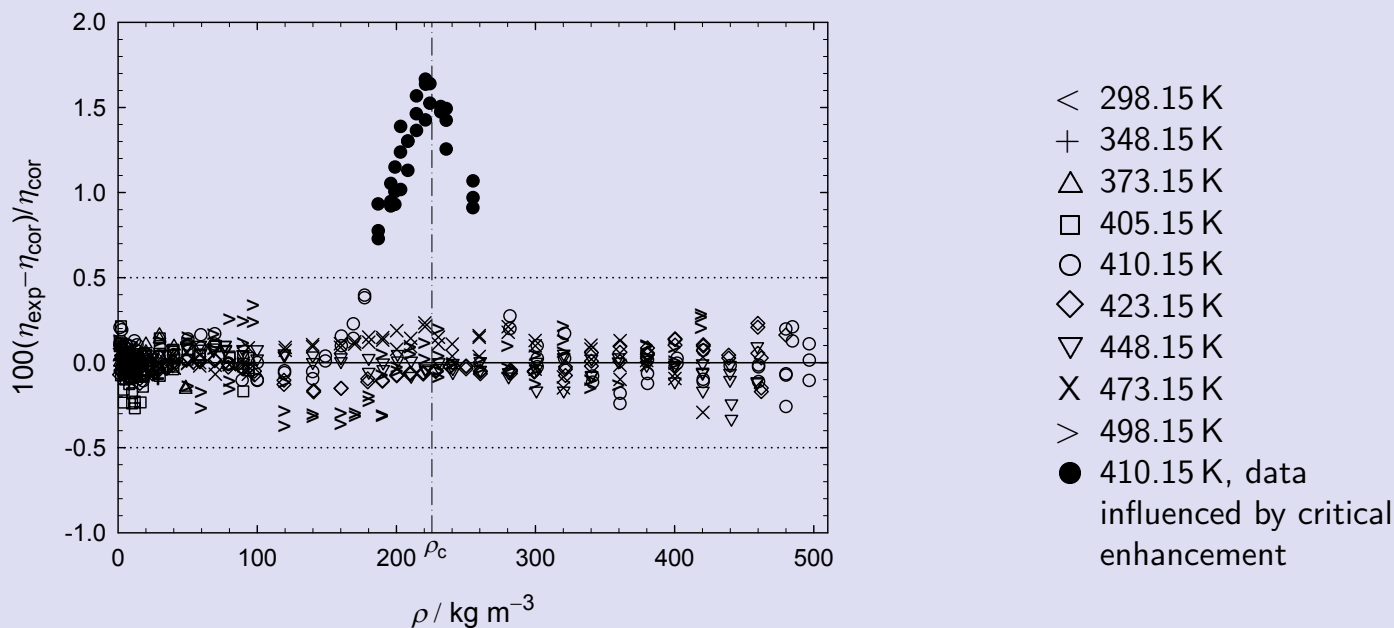


¹¹ Diller, D. E. and van Poolen, L. J., *Int. J. Thermophys.* **6**, 43-62 (1985).

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



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 \rightarrow 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.*) \rightarrow 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

- Reduced quantities: $\tau = \frac{T_c}{T}$, $\delta = \frac{\rho}{\rho_c}$
- Separate zero-density viscosity and initial-density dependence correlation as before
- Bank of terms for the higher-density terms and the critical region:

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

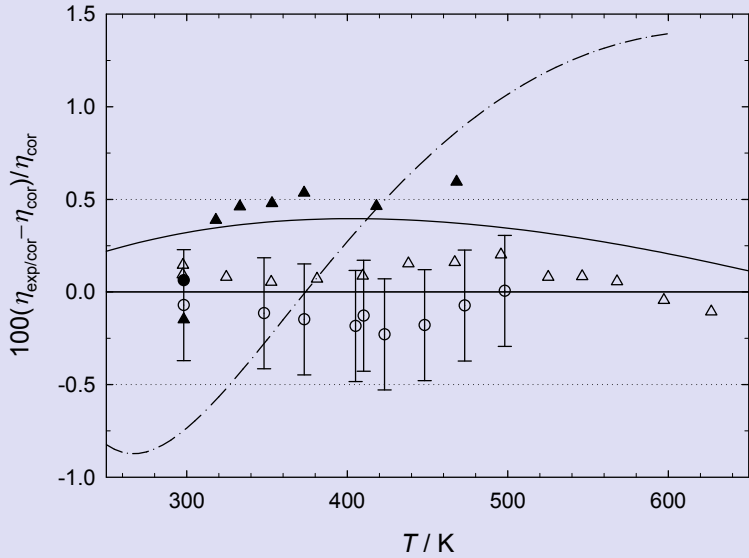
- Final result for isobutane:

$$\begin{aligned} \eta_{\text{cor}, i-C_4H_{10}}(\tau, \delta) &= \eta_0(\tau) + \eta_1(\tau)\delta + \sum_{i=1}^{10} A_i \tau^i \delta^i + \tau^{1/2} \delta^{-2/3} A_{11} (\delta^{5.6} \tau)^4 \\ &+ \sum_{i=12}^{13} A_i \tau \delta e^{-\beta_i (\delta - 1)^2 - \varepsilon_i |\tau - 1|} . \end{aligned}$$

Comparison equation vs. experiment and correlations

Viscosity in the limit of zero density and at low densities

- Agreement within the experimental uncertainty
- Error bars: $\pm 0.3\%$



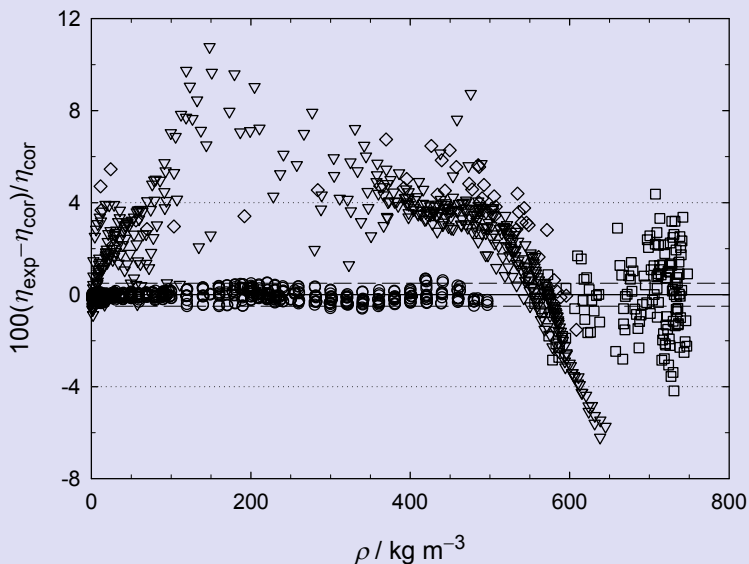
- \triangle, \circ experimental data in the limit of zero density
- \blacktriangle, \bullet experimental data at atmospheric pressure
- - - correlation by Younglove and Ely (1987)¹⁴
- correlation by Vogel *et al.* (2000)

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

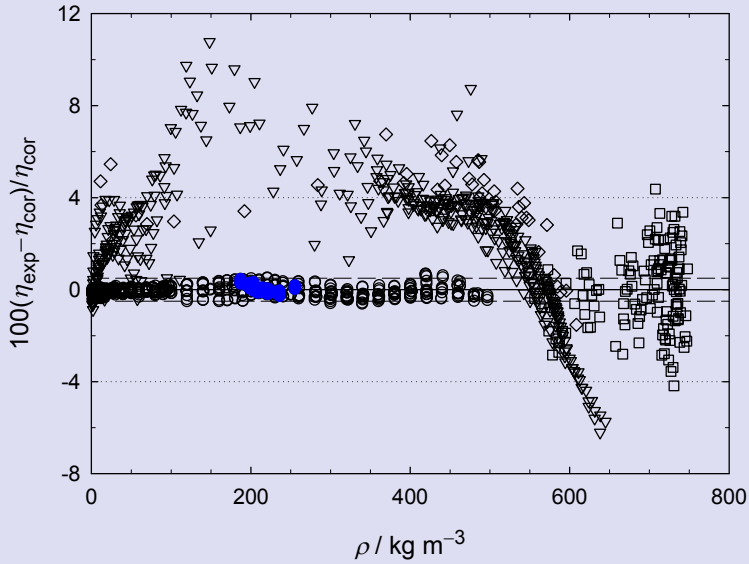


- $\nabla, \diamond, \square$ earlier experimental data
- \circ new experimental data

Comparison equation vs. experiment

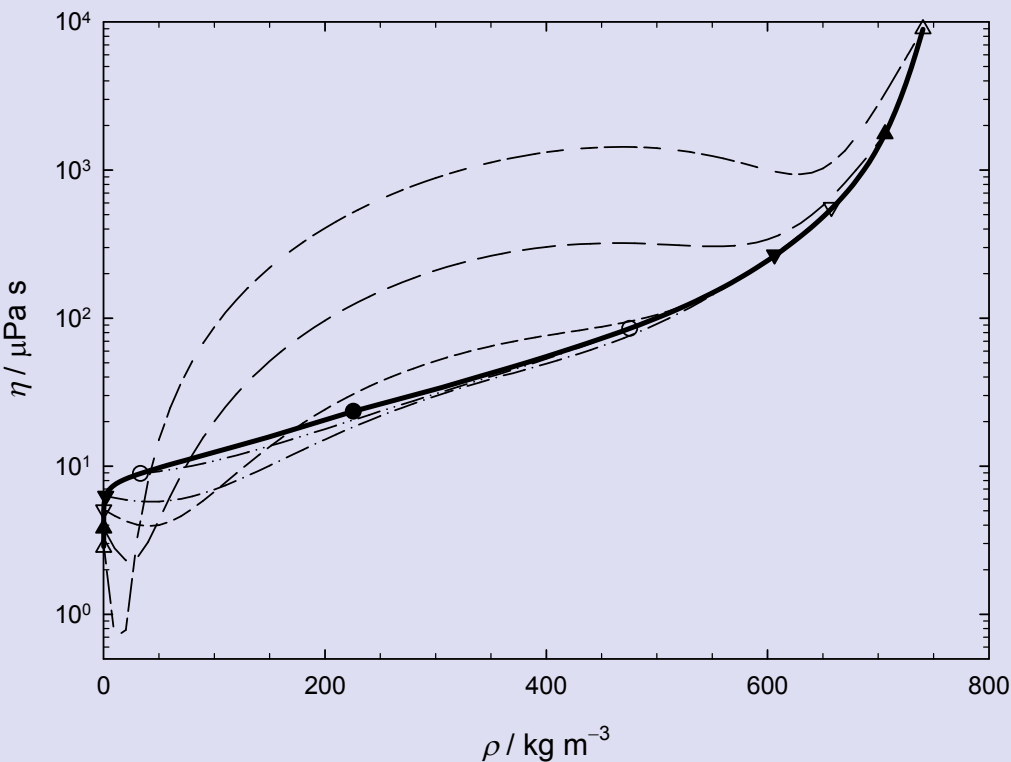
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▽, ◇, □ earlier experimental data
○ new experimental data

Behavior in the two-phase region



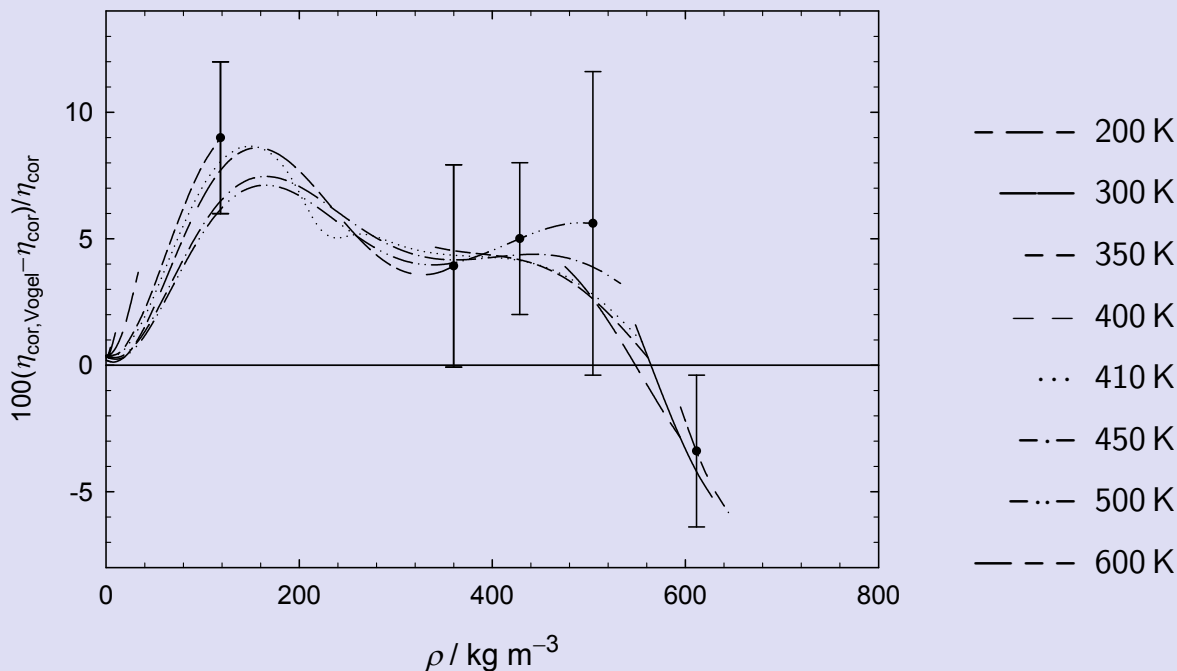
△ triple point
● critical point
— saturated-vapor and saturated-liquid curves

△ - - - △ 113.73 K
▲ - - - ▲ 150 K
▽ - - - ▽ 200 K
▼ - - - ▼ 250 K
○ - - - ○ 350 K

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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